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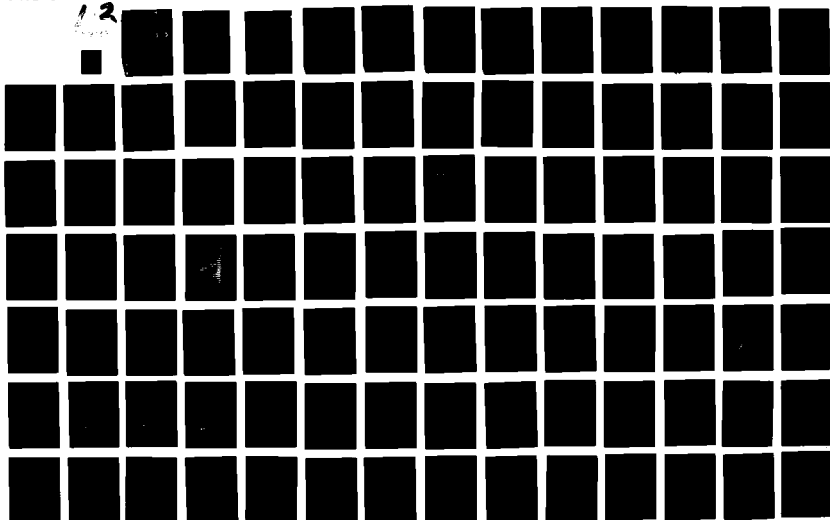
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TEMPORAL, DIRECTIONAL, AND SPATIAL VARIABILITY OF WET DEPOSITION
IN THE NORTHEASTERN UNITED STATES

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Final report - *APRIL 1981*

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Doctor of Philosophy.

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The data of the MAP3S and NADP networks for 1979 were also used to develop spatial distributions of normalized and estimated wet deposition for the eastern United States. A rather uniform pattern in normalized wet deposition for sulfate and nitrate emerges, lending support to the concept that the deposition of these materials is not confined to any particular region.

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WET DEPOSITION IN THE NORTHEASTERN UNITED STATES

by

Jerre W. Wilson

A DISSERTATION

SUBMITTED TO THE STATE UNIVERSITY OF NEW YORK AT ALBANY

IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

COLLEGE OF SCIENCE AND MATHEMATICS

DEPARTMENT OF ATMOSPHERIC SCIENCE

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The precipitation chemistry data base of the Multistate Atmospheric Power Production Pollution (MAP3S) and the National Atmospheric Deposition Program (NADP) were examined for temporal, spatial, and directional variability of wet deposition of the dominant ions in precipitation for selected sites in the northeastern United States.

Sulfate ($\text{SO}_4^{=}$), Hydrogen (H^+), and Ammonium (NH_4^+) ions exhibited a distinct summer maxima in both concentration and deposition, while Nitrate (NO_3^-) remained relatively constant throughout the years 1977-1979. Linear regression analysis applied to the three year cumulative totals was found to provide a reasonable wet deposition prediction capability.

The Air Resources Laboratories - Atmospheric Transport and Dispersion (ARL-ATAD) trajectory model was used to examine directional or sector variability and to characterize individual events as to air mass origin, as determined by 48 hour back trajectories. Case studies were examined to illustrate variability in the chemical quality of precipitation from air masses passing over distinctly different regions in the United States and Canada. The directional variability in wet deposition of all ions was found to coincide with the distribution of precipitation.

The data of the MAP3S and NADP networks for 1979 were also used to develop spatial distributions of normalized and estimated wet deposition for the eastern United States. A rather uniform pattern in normalized wet deposition for sulfate and nitrate emerges, lending

support to the concept that the deposition of these materials is not confined to any particular region. An increased gradient in normalized $\text{SO}_4^{=}$ and NO_3^{-} deposition was found in the area of the Appalachian Mountains indicating topography may affect the distribution of low level pollutants along the eastern United States.

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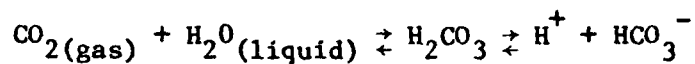
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1.0 HISTORICAL REVIEW OF PRECIPITATION CHEMISTRY MEASUREMENTS

In recent years precipitation chemistry, and acid precipitation in particular, has attracted attention in the scientific community as well as the general public. Acid precipitation is generally accepted as an international phenomena, thus stimulating cooperation between various countries and organizations.

The most accepted definition of acid precipitation is that which has a pH below 5.6, or the lowest pH that could be produced by carbonic acid if pure water were in equilibrium with atmospheric carbon dioxide at 25°C (Barrett and Brodin, 1955). This equilibrium is expressed by:



However, generally and particularly in cases of "rain with high acidity" a significant amount of H^+ present is attributable to other components including sulfuric and nitric acids (Cooper et al., 1976).

The European community was the first to recognize the need for chemical analysis of the air and precipitation. John Evelyn in 1661 was one of the first researchers to address atmospheric pollution and proposed solutions to the problem which included taller chimneys, increased distance between source and receptor, consideration of prevailing winds, and topographic obstacles. Miller (1905) credits Marggraf with conducting the earliest precipitation chemistry measurements of rain and snow in Berlin, 1761-1767, in which he measured nitric acid, chlorine, and lime.

However, it wasn't until the middle of the 19th century that a concerted effort was undertaken to establish monitoring networks and seriously study air quality. Marchand (1852) recognized the need to include both rain and snow to provide the complete annual description of precipitation chemistry. Chatin (1852) noted an increased chlorine content in the rain with maritime trajectories as origin and also proposed dew and mist as deposition mechanisms.

Robert Angus Smith (1872) published an extraordinary work entitled Air and Rain: The Beginnings of a Chemical Climatology in which he first used the terminology "acid rain." This comprehensive text examines precipitation chemistry at various global locations, air quality at various locations and environs, and the effect of both air and water pollution. The work of Smith is especially noteworthy not only because it provides an early history of spatial variability in precipitation chemistry, but it is also extremely comprehensive in that the analysis includes sulphates, ammonia, nitric acid, free acid, and chlorides as illustrated in Table 1.

One of the main thrusts of the work of Smith was to show the variability of air and water quality, particularly between rural and city environments as shown in Table 2.

Unfortunately, the work of Smith went essentially unnoticed until recently when he received the credit he so rightly deserves.

Around 1850 a monitoring network was established at Rothamsted, England, which provided a continuous source of precipitation chemistry measurements for the next 50 years. Lawes et al. (1881, 1883) were the first to present a detailed report of these collections by

TABLE I
 Manchester Rain-Water Collected during 1869
 Acids (Combined and Free) and Acidity

Date		Hydrochloric Acid		Sulphuric Acid (Anhydrous)		Proportion- Hydrochloric to Sulphuric Acid	Acidity Calculated as Sulphuric Acid (Anhydrous)	
		Grains per Gallon	Parts per Million	Grains per Gallon	Parts per Million		Grains per Gallon	Parts per Million
January	(a)	.5110	7.30	5.6000	80	1 to 10.96	2.3087	32.98
February	"	.6387	9.12	2.9400	42	1 " 4.60	1.6930	24.20
March	"	.7300	10.43	7.3500	105	1 " 10.07	1.3664	19.52
April	"	.3006	4.29	3.6750	52.50	1 " 12.22	.5465	7.81
May	"	.3193	4.56	2.9400	42	1 " 9.20	1.4347	20.49
June	"	.5677	8.11	3.2666	46.67	1 " 5.75	.9565	13.66
July	"	.3931	5.62	3.2666	46.67	1 " 8.31	.4782	6.83
August	"	.3006	4.29	2.9400	42	1 " 9.78	.7857	11.22
"	(b)	.1460	2.08	2.9400	42	1 " 20.14	None	None
"	(c)	.2044	2.92	1.7294	24.71	1 " 8.46	-	-
September	(a)	.3407	4.87	3.2667	46.67	1 " 9.59	.4441	6.34
"	(b)	.2555	3.65	1.9600	28	1 " 7.67	None	None
"	(c)	.2044	2.92	.9800	14	1 " 4.79	.0683	.98
October	(a)	.4258	6.08	3.7800	54	1 " 8.88	1.1273	16.10
"	(b)	.3931	5.61	1.5474	22.11	1 " 3.94	.1366	1.95
"	(c)	.5678	8.11	1.5474	22.11	1 " 2.72	.1366	1.95
November	(a)	.7862	11.23	2.9400	42	1 " 3.74	.3074	4.39
"	(b)	.7300	10.43	4.2000	60	1 " 5.73	.0842	.49
"	(c)	.6012	8.60	1.4700	21	1 " 2.44	.1025	1.46
December	(a)	.1022	1.46	.9187	13.12	1 " 8.99	.1879	2.68
"	(b)	.3194	4.56	2.9400	42	1 " 9.20	.3416	4.88
"	(c)	.2222	3.17	1.9600	28	1 " 8.82	.3758	5.37
Mean		.4118	5.88	2.9163	41.66	1 to 7.08	.5833	8.33
Mean of (a)		.4513	6.45	3.5736	51.05	1 " 7.91	.9697	13.85
Mean of (a) from August		.3911	5.59	2.7691	39.56	1 " 7.08	.5705	8.15
Mean of (b)		.3688	5.27	2.7175	38.82	1 " 7.37	.1025	1.46
Mean of (c)		.3600	5.14	1.5373	21.96	1 " 4.27	.1708	2.44

(a) Behind the laboratory, 12 ft. above the ground

(b) Same place, 30 ft. above the ground

(c) Behind the Literary and Philosophical Society, George Street, 2 ft. above the ground

TABLE 1. Manchester rain-water collected during 1869. (Smith, 1872)

Averages. Hydrochloric Acid (Chlorides)

4

<u>Rain Obtained from</u>	<u>Grains per Gallon</u>	<u>Parts per Million</u>
Darmstadt	.0681	.97
London, specimens for 1869	.0872	1.25
German specimens	.0919	1.31
Birkenhead, Liverpool	.2217	3.17
Scotland - Inland country places	.2357	3.37
Near an Alkali Works	.2380	3.40
England - Inland country places	.2795	3.99
Manchester, 1870	.4055	5.79
Manchester, average of 1869 and 1870	.4086	5.83
Scotland - towns (Glasgow not included)	.4102	5.86
Manchester, 1869	.4118	5.88
Newcastle-on-Tyne	.5678	8.11
England - towns	.6093	8.70
Glasgow	.6282	8.97
St. Helen's	.6670	9.53
Liverpool	.7110	10.16
Scotland - Seacoast country places, west	.8600	12.28
Scotland - Seacoast country places, average of east and west	.8819	12.59
Scotland - Seacoast country places, east	.9039	12.91
Runcorn	1.8022	25.74
Waterloo, near Liverpool	2.5550	36.50
Ireland - Valentia	3.4067	48.67
England - Seacoast country place, west (only one)	3.9308	56.15

Averages. Sulphuric Acid (Sulphates)

<u>Rain Obtained from</u>	<u>Grains per Gallon</u>	<u>Parts per Million</u>
Scotland - Inland country places	.1444	2.06
Ireland - Valentia	.1911	2.73
Scotland - Seacoast country places, west	.2529	3.61
England - Inland country places	.3865	5.52
Scotland - Seacoast country, avg. of E and W	.3947	5.64
England - Seacoast (west) country	.4116	5.88
Scotland - Seacoast country places, east	.5366	7.66
Waterloo, Liverpool	.8004	11.43
German specimens	1.1481	16.40
Scotland - towns (Glasgow not included)	1.1553	16.50
London, 1869	1.4345	20.49
Birkenhead, near Liverpool	1.6210	23.16
Runcorn	1.6537	23.62
Darmstadt - Germany	2.0417	29.17
St. Helen's	2.3232	33.19
England - towns	2.3988	34.27
Liverpool	2.7714	39.59
Manchester, 1869	2.9163	41.66
Newcastle-on-Tyne	3.1111	44.44
Manchester, average of 1869 and 1870	3.1378	44.82

TABLE 2. Average chloride and sulfate in precipitation.
(Smith, 1872)

studying daily and monthly concentrations of nitrogen, ammonia, and sulfuric acid. Although they noted the direction of the wind at the time of collection, correlations between daily concentrations and direction were inconclusive. Sulfuric acid deposition was found to be equally distributed between winter and summer while two-thirds of the chlorine was deposited during the winter months. The average value for SO_3 averaged over two years was 2.41 ppm amounting to 18.5 lbs. deposited per acre per year. The winter chlorine deposition maximum was later verified by Kinch (1887, 1900) with the winter/summer ratio being approximately 1.5 averaged over 26 years.

Miller (1905) continued the work at Rothamsted, as well as compared nitrogen, chlorine, and sulfuric acid for various locations and demonstrated large global variations in concentration and deposition as shown in Tables 3-5.

Crowther and Ruston (1911) showed that "smoke-infested localities" such as Garforth, England, exhibit considerably higher average deposition values than do the relatively clear rural environments such as Rothamsted, with sulfur deposited being five times higher. Coal combustion was proposed as the mechanism for the increased level of impurities. Free acid was also examined producing evidence that winter rainfall was twice as acidic as summer for that locale due to the highly acidic fogs that linger in the winter months. The increased level of free acid in the atmosphere was also found to have a detrimental effect on plants by direct action and indirectly reducing ammoniacal fermentation of the soil humus.

Nitrogen as Ammonia and Nitric Acid in Rain

	Date	Rainfall (inches)	Per Million					Per Acre Per Annum					% of Total		
			as NH ₃	as N ₂ O ₅	as NH ₃	as N ₂ O ₅	as NH ₃	as N ₂ O ₅	Total (lb.)	as NH ₃	as N ₂ O ₅	as NH ₃	as N ₂ O ₅	as NH ₃	as N ₂ O ₅
Rothamsted	1888-9 1900-1	27.25	0.440	0.183	2.71	1.13	3.84	70.6	29.4						
Copenhagen (114)	1880-5	21.95	1.97	0.473	9.27	2.21	11.48	80.8	19.2						
Gembloux (93)	1889-91	27.23	1.143	0.345	7.07	2.14	9.21	76.8	23.2						
Montsonris (67)	1876-1900	21.52	2.13	0.66	10.37	3.22	13.59	76.3	23.7						
Mettay (66)	1877	29.90	0.409	-	2.77	-	-	-	-						
Dahme (39)	1865	17.09	1.42	0.30	5.50	1.16	6.66	82.6	17.4						
Ida-Marienhutte (25)	1865-70	22.65	-	-	-	-	9.92	-	-						
Instertburg (39)	1864-6	25.67	0.65	0.38	3.90	2.25	6.15	63.1	36.9						
Kuschen (39)	1864-6	14.78	0.48	0.16	1.63	0.55	2.18	75.0	25.0						
Proskan (39)	1864-5	17.81	3.21	1.73	12.94	6.97	19.91	65.0	35.0						
Regenwalde (39)	1864-7	22.72	2.08	0.62	10.69	3.28	13.97	77.0	23.0						
Rostock (53)	1880-1	33.27	0.892	-	6.73	-	-	-	-						
Florence (11)	1869-75	38.31	1.004	0.57	8.70	3.09	11.79	73.8	26.2						
Vallembrosa (11)	1872-5	59.89	0.617	0.253	8.36	3.46	11.82	70.7	29.3						
Scandicci (90)	1888-90	29.18	0.614	0.266	4.06	1.76	5.82	69.8	30.2						
Catania (10)	1888-9	18.36	0.327	0.161	1.36	0.67	2.03	66.9	33.1						
St. Michele, Tirol (69)	1885-6	43.93	1.188	0.579	11.83	5.76	17.59	67.3	32.7						
Libwerd, Bohemia	1877-8	24.41	1.3	0.61	7.18	3.37	10.55	68.1	31.9						
Pecok	1883-4 to 1885-6	19.34	1.26	0.50	5.53	2.19	7.72	71.6	28.4						
Ploty (122)	1900-3	17.49	0.854	0.061	3.38	0.24	3.62	93.3	6.7						
Pretoria (113)	1904	-	0.68	0.12	-	-	-	85.1	14.9						
Tokyo (59)	1883-4 1885	52.67 62.28	- 0.126	0.093	- 1.77	1.11	2.88	61.6	38.4						
New Zealand (51)	1884-8	29.70	0.076	0.169	0.50	1.13	1.63	30.7	69.3						
Kansas (42)	1887-9	29.41	0.393	0.154	2.62	1.03	3.64	71.8	28.2						
Mississippi (112)	1894-5	44.11	0.235	0.074	2.35	0.74	3.09	76.0	24.0						
Calcutta	1891	46.01	0.172	0.115	1.79	1.20	2.99	59.7	40.3						
Madras	1888-93	39.21	-	-	-	-	1.91	-	-						
Ceylon (4)	1898-9	82.13	0.196	0.069	3.65	1.28	4.93	72.0	28.0						
East Java (75)	1891	(47)	0.11	0.06	1.13	0.71	1.84	61.5	38.5						
Mauritius (21)	1895	(70)	0.43	0.40	6.81	6.34	13.15	51.8	48.2						
Reunion (88)	1886-7	(40)	-	0.69	-	6.24	-	-	-						
Barbados (5)	1885-97	63.95	0.084	0.268	1.22	3.88	5.10	23.9	76.1						
Venezuela (71 and 88)	1883-5	(40)	1.55	0.58	14.03	5.20	19.23	72.8	27.2						
British Guiana (52)	1890-1900	102.41	0.055	0.078	1.17	1.82	2.99	39.1	60.9						
Campinas (30)	1890	-	0.99	-	-	-	-	-	-						

TABLE 3. Nitrogen as ammonia and nitric acid in rain (Miller, 1905)

TABLE 4

Nitrogen as Nitrous and Nitric Acids in Rain and Snow

Rainfall (inches)		Nitrogen				Per Acre	
		Per Million		as Nitrates		as Nitrites	as Nitrates
		Min.	Max.	Mean	Min.	Max.	Mean
St. Chamas (31)	(20)	0.0	0.316	0.133	0.001	0.716	0.162 (0.60)
St. Chamas (snow)	-	-	-	0.250	-	-	-
Langres (31)	-	-	-	0.270	-	-	0.881
Scandicci (90)	27.28	0.0	0.0168	0.0045	0.033	0.729	0.255
Catania (10)	18.36	0.0001	0.0027	0.0006	0.035	0.244	0.161
Ploty (122)	17.49	0.0	0.025	0.011	0.002	0.178	0.050
							0.043
							0.197

TABLE 5

Chlorine and Sulphuric Acid in Rain

	Date	Rainfall (inches)	Per Million			Per Acre			SO ₃ to 1 Cl
			Chlorine		Sulfuric Acid	Chlorine (lb.)	Sulphuric Acid (lb.)		
			Min.	Max.				Mean	
Rothensted	1877-8	28.78	0.40	20.10	2.28	2.57*	14.87	17.41*	1.19
	1900-1								
Cirencester (60)	1874-1900	30.61	1.15	10.38	3.17	-	21.90	-	-
Scandicci (91)	1889-91	27.67	0.17	31.95	5.63	-	35.35	-	-
Perugia (14)	1886-7	33.96	1.38	40.28	3.15	-	24.22	-	-
Catania (10)	1888-9	18.36	1.47	7.36	5.48	5.02	22.79	20.89	0.92
LaGuardia (79)	1892-3	56.42	7.1	71.9	31.2	-	399.5	-	-
New Zealand (51)	1884-8	29.70	2.6	36.4	8.83	2.22	59.44	14.94	0.25
Barbados (5)	1885-97	63.95	3.55	33.97	8.14	-	127.8	-	-
British Guiana (52)	1890-1900	102.41	(1.68)	(17.68)	5.04	-	116.88	-	-
Caylon (4)	1898-9	82.13	-	-	9.72	-	180.63	-	-
Calcutta	1894	46.01	1.82	5.44	3.16	-	32.87	-	-
Madras	1888-93	39.21	-	-	4.08	-	36.27	-	-

*1881-87

Masson et al. (1917) found that the amount of rainfall in Australia varied inversely with the concentration of oxidized nitrogen while there was no correlation between the total amount of nitrogen and total rainfall.

North American researchers also recognized the need to study precipitation chemistry. Shult et al. (1917) found a maximum nitrogen deposition in April and May in Ottawa, Canada, and surmised this was beneficial since crops were normally fertilized at this time. However, no consideration was given to the fact that the high levels of nitrogen might be a result of the fertilization. MacIntire and Young (1923) found no evidence that precipitation depleted the soil of bases in Tennessee and also suggested it might even be beneficial. Potter (1930) was one of the first researchers to present his results in terms of pH when reporting his measurements of rain, potable water, and water collected from plants in New England. His values ranged from 5.0 to 7.6 with the lowest values being from potable water.

It became apparent that individual efforts would not be able to provide the complete picture of precipitation chemistry from source to receptor. Scandinavian researchers were the first to recognize the potential environmental impact of acid precipitation, formulate a comprehensive monitoring network, and carefully analyze data. The first organized Scandinavian network was established by Torstensson, Egner, and Angstrom (Emanuelson, Eriksson, and Egner, 1954) and consisted of 28 stations located primarily in southeastern Sweden. This network collected monthly samples during the period October 1, 1947 to September 30, 1950. Eriksson (1952a, 1952 b) used this network to

develop a relationship between natural and anthropogenic sources of gases and aerosols. Barrett and Brodin (1955) used the data of this rural Scandinavian network to obtain spatial and temporal variations of the acid-alkaline balance of precipitation. Southern Scandinavia was found to be more acidic, particularly during winter months at the time of maximum combustion of fossil fuels and southerly flow from the European continent. This was one of the first proposals of long range transport of pollutants across international boundaries and thereby firmly established acid precipitation as a regional or synoptic problem.

In 1954 the rural Scandinavian network was expanded to include the British Isles as well as all of Scandinavia (Egner and Eriksson, 1955). This marked the first international cooperation on acid precipitation monitoring. This network was later expanded to include stations in France, Germany, and the Soviet Union. This network showed an increased concentration of both sulfate and nitrate. Based on these data Granat (1972) developed a model based on a stoichiometric relation between acids and bases to interpret the amount of acid found in precipitation and predict future depositions of acid by precipitation. Munn and Radke (1971) used the data of two of the Scandinavian stations to study the influence of synoptic weather patterns on the chemical composition of monthly precipitation samples. They found a definite correlation between chloride deposition and frequency of rain-bearing flows in the SSW-NW sector and between sulfur deposition and rain-bearing flows in the SE-SW-NW sector implicating the heavily industrialized regions of England and northern Germany.

Selezneva (1972) used a Russian network similar to that of the Scandinavian system to estimate the background concentrations for different geographical regions of the USSR. He estimated that the background levels account for 30-40% of the total contamination and local sources contribute the remaining 60-70% of which 20-30% are natural sources and the remainder being of anthropogenic origin.

European results regenerated research interest in the United States with Houghton measuring the pH of rain at Brookline, Maine, in 1939 (Likens, 1975). He obtained a value of 5.9 for a single rain-storm. In 1949 Landsberg (1954) measured precipitation pH and obtained for individual raindrops a mean value of 4.2. In 1952-53 Landsberg measured a mean value of 4.0 for a large number of storms near Boston, Massachusetts. Herman and Gorham (1957) analyzed precipitation at Kentville, Nova Scotia during the period 1952-54 and found an average value of a pH of 5.7 for all types of precipitation sampled.

Prior to 1955 all precipitation chemistry measurements, both American and European, were ground-based well within the boundary layer. Houghton (1955) was the first to recognize that the pH could change between cloud water and that of the precipitation collected at the ground. He made fog and cloud water measurements at four northeastern U.S. sites within the boundary layer and one above the boundary layer located at Mount Washington, New Hampshire. His cloud water pH measurements varied from 3.0 to 5.9 with a mean of 4.5, while his mean value of 7.2 for the coastal regions of New England was considerably more than that of Herman and Gorham (1957).

The first comprehensive United States network consisting of 67 stations was organized by Junge and operated from July 1955 through July 1956. Junge (1958) and Junge and Gustafson (1956) utilized this network to compute the distribution of ammonia, nitrate, and chloride over the United States during this period. Junge and Werby (1958) later presented concentrations of sodium, potassium, calcium, and sulfate and estimated the average global residence time of SO_4 to be 40 days. Although the Junge network presented data on the majority of the constituents normally considered in precipitation chemistry studies, it failed to record hydrogen and magnesium ions. Cogbill and Likens (1974) attempted to fill this data void by using chemical mass balancing techniques to calculate the pH of the northeastern United States based on the data of the Junge network. Their work established the presence of acid precipitation prior to 1955.

The establishment of the Hubbard Brook Experimental Forest in New Hampshire in 1963 provided an excellent opportunity to study the effect of industrialized centers on the rural environment. Since Hubbard Brook has operated for over 10 years, it provides the most comprehensive record of precipitation chemistry in the United States. All measurements were of precipitating clouds with instruments based well within the planetary boundary layer. Based on these measurements Likens et al. (1976) found that sulfate and hydrogen dominated the Hubbard Brook region, with $\text{SO}_4^{=}$ being 2.5 times more prevalent than the next most abundant anion and the hydrogen 5.9 times more common than the next most abundant cation. He characterized the precipitation at Hubbard Brook as a contaminated solution of sulfuric and nitric acid with a pH of about 4.1.

The composition of rainfall from the work of Likens et al. averaged over an 11 year period at the Hubbard Brook Experimental Forest, New Hampshire, is presented in Table 6.

The sum of the concentrations of the anions ($97.5 \mu\text{eq/liter}$) is nearly equal to the sum of the concentrations of cations ($105.6 \mu\text{eq/liter}$). The standard deviations of the sums ($\pm 3.5 \mu\text{eq/liter}$) are small enough so that the difference between them is significant at the one sigma level of confidence. It is therefore possible that other unidentified anions with total concentrations on the order of $1.5\text{--}16.0 \mu\text{eq/liter}$ might be present. Likens et al. was one of the first investigators in the United States to maintain a carefully supervised and quality controlled precipitation chemistry network dedicated to determine the flow of material from the atmosphere into a calibrated watershed. Likens et al. observed that there has been a slight upward trend in concentration of hydrogen ions between 1964-1965 and 1970-1971, followed by a downward trend until 1973-1974; overall (1964-1974), however, no trend in concentration is statistically significant (see Figure 1).

A different result was obtained by Dovland et al. (1976) from pH measurements at three Norwegian stations, shown in Figure 2. The decrease, especially in the beginning of the sixties, is quite evident. However, as pointed out by Perhac (1980), British statisticians from the Central Electricity Generating Board have examined the pH data in Figure 2, and found no trend from 1955 to 1964 and none from 1965 to 1977. The cause of the sudden change of pH in 1964-1965 is not known. Changes in method of sample collection (which did happen), the use of

TABLE 6

Composition of Rainfall

(The units are microequivalents per liter of liquid precipitation)

<u>Species</u>	<u>Quantity μeq/liter</u>
SO_4^{--}	59.7
NO_3^-	23.1
Cl^-	14.4
PO_4^{--}	0.25
H^+	73.9
NH_4^+	12.1
Ca^{++}	8.6
Na^+	5.4
Mg^{++}	3.7
K^+	1.9

$$\text{ratio} \frac{\text{H}^+ + \text{NH}_4^+}{\text{SO}_4^{--} + \text{NO}_3^-} = 1.04$$

$$\text{Ca}^{++} + \text{Mg}^{++} = 12.3$$

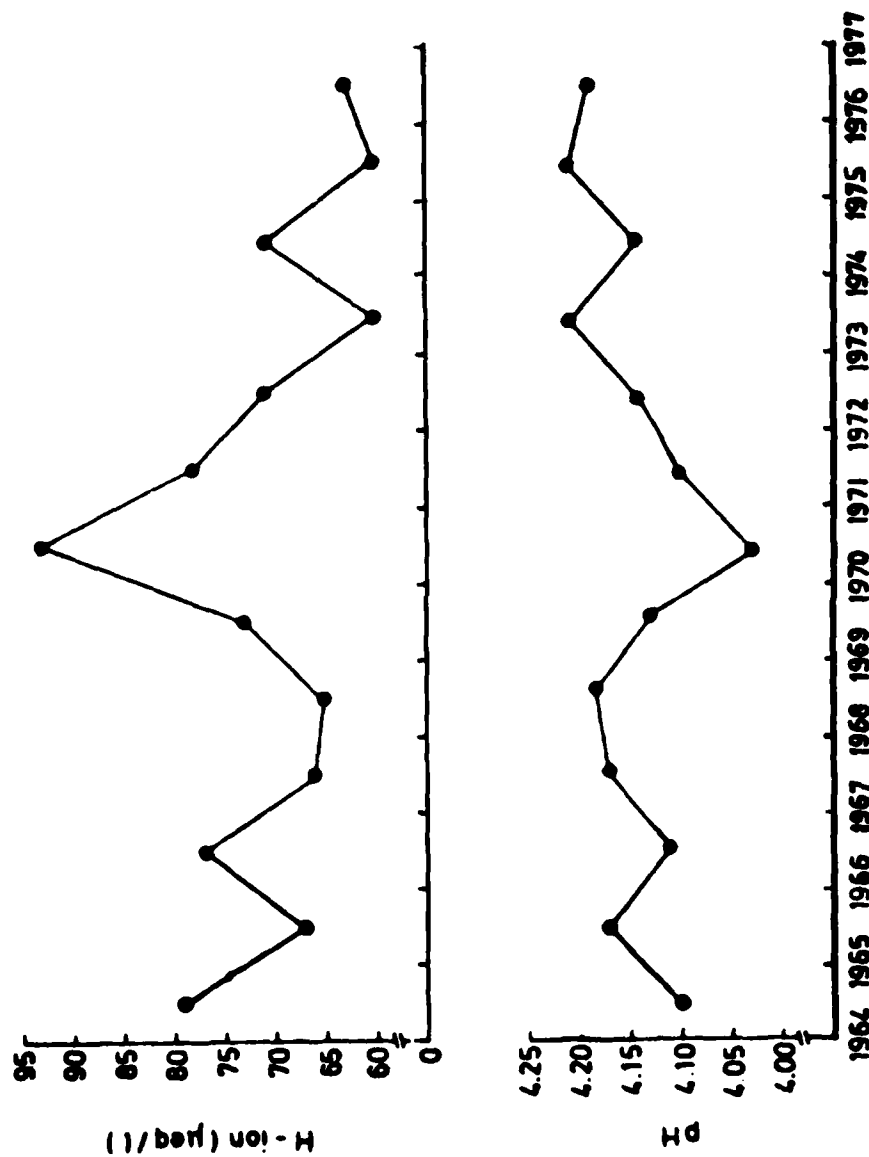


Figure 1. Annual hydrogen ion concentration and pH of precipitation (weighted for volume) at the Hubbard Brook Experimental Forest Farm, 1964 to 1977. (Likens et al., 1980)

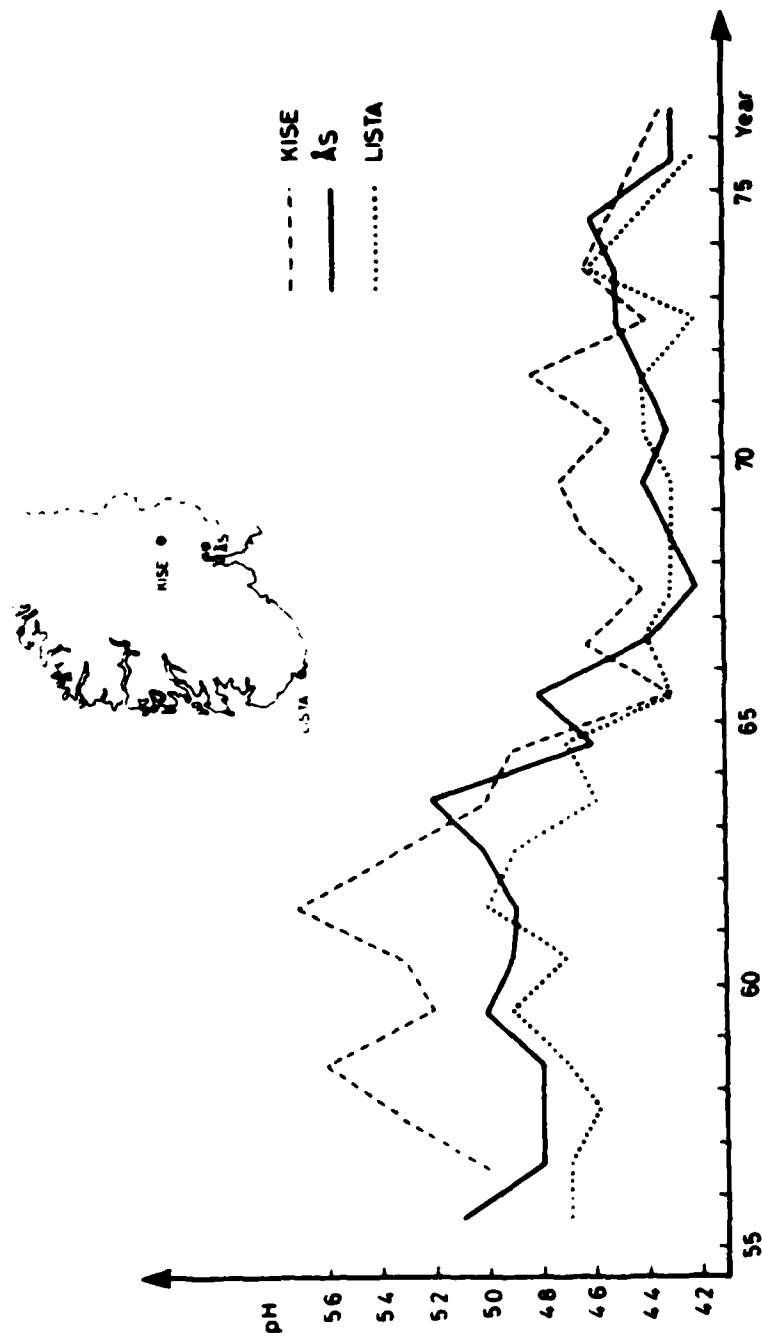


Figure 2. Time variation of annual mean pH of precipitation at three Norwegian stations. The annual mean pH is determined from the total deposition of H^+ divided by the amount of precipitation. (Seip and Tollan, 1978)

different analytical techniques, or changes in natural or anthropogenic emissions are factors to be considered. The average concentration of major ions in the precipitation at two Norwegian sites are presented in Table 7 (Johannessen and Horanger, 1976). It is argued in the OECD (1977) report that a major part of the sulfur compounds deposited in Norway may be traced back to fossil fuel combustion in other European countries.

The knowledge of pH in precipitation is one important atmospheric chemistry parameter, but certainly not the only one. More important to know, however, is the total composition of the precipitation as was pointed out earlier. Knowledge of ion composition allowed Cogbill and Likens (1974) to calculate the pH for the 24 sites in the eastern United States where Junge collected precipitation with wet-only collectors in 1955-56. The resulting pH isolines are shown in Figure 3.

A large area of the northeastern United States was subjected to acid precipitation by the mid-1950s.

The National Center for Atmospheric Research organized the National Precipitation Sampling Network and collected data on a monthly basis from 33 locations across the United States from 1960 to 1966 (Lodge et al., 1968) using wet-only, automatic collectors. The pH values were not included in the final report, but Cogbill and Likens (1974) again used chemical balancing techniques with the combined data of Lodge et al. (1968), Gambell and Fisher (1966), and Pearson and Fisher (1971) to calculate pH for the eastern United States for 1965-66. The vast majority of monthly pH values for stations west of the Mississippi River were consistently greater than

TABLE 7

Average Concentrations (neq/liter) of Major Ions in the Precipitation at
Birkenes in Aust-Agder County (June 1972 to June 1977)
and Treungen in Telemark County (September 1973 to June 1975)

	<u>Birkenes*</u>	<u>Treungen</u>
H ⁺	65	52
Ca	15	7
Mg	17	6
Na	79	26 ^a
K	7	2
NH ₄	41	26
SO ₄	88	59
Cl	61	22
NO ₃	44	27

^aCalculated from the Mg concentration using the Na/Mg ratio in seawater

$\frac{H^+ + NH_4^+}{SO_4^{2-} + NO_3^-} =$	0.8	0.9
$Ca^{++} + Mg^{++} =$	32	13

*Birkenes is located close to the coast.

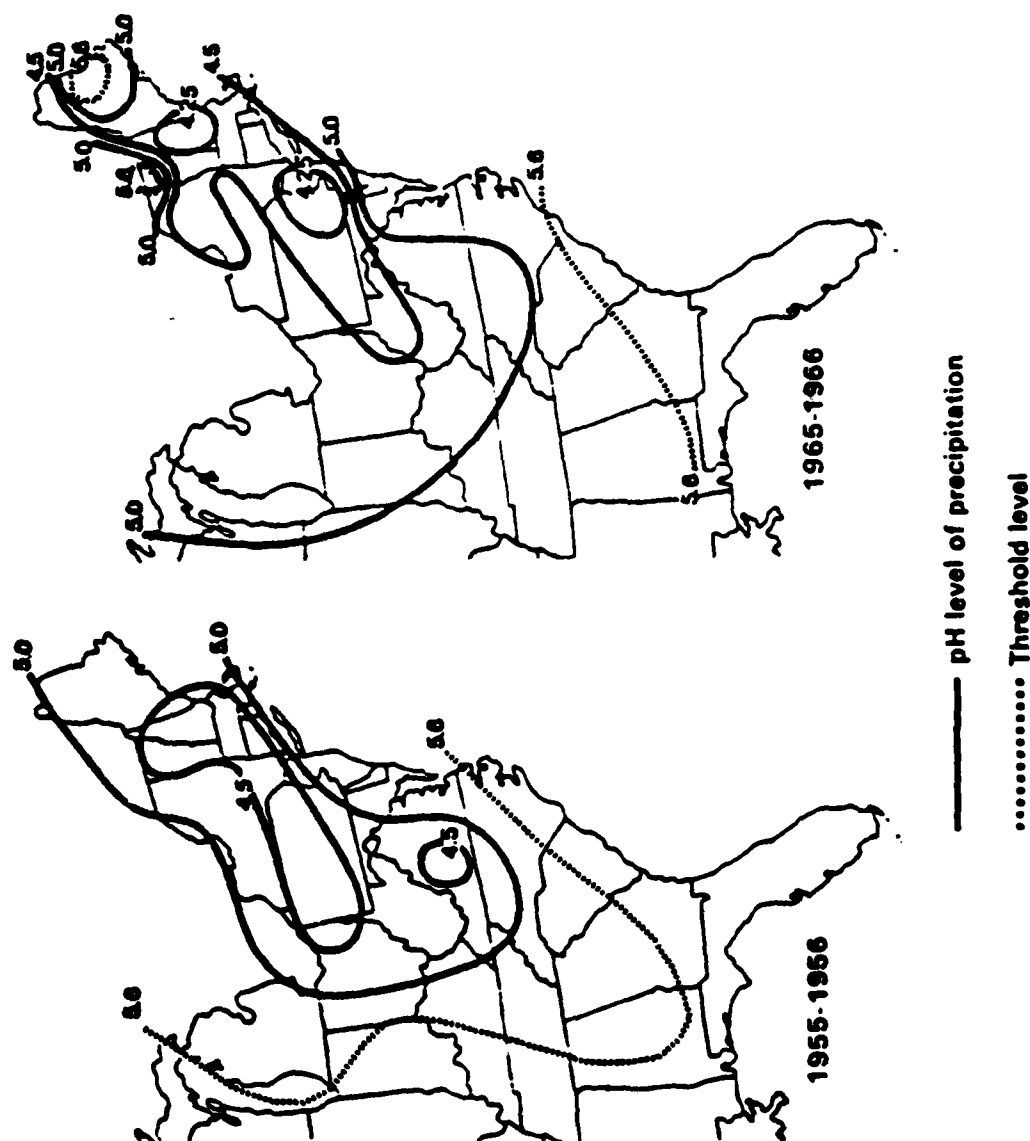


Figure 3. Comparisons of pH for 1955-1956 and 1965-1966. (Cogbill, 1975b)

5.6. In contrast, monthly values east of the Mississippi River were much more acidic as shown in Figure 3. A comparison of the 1955-56 and 1965-66 isopleths prepared by Cogbill and Likens (1974) shows a marked increase in acidity over the entire eastern half of the United States from 1955 to 1966, with New England being the most acidic region. This alleged spreading of the area affected by acid precipitation was recently questioned by Perhac (1980) on the basis one should use data for trend analysis only from stations which are the same for the different time period. In comparing the 1955-56 and 1965-66 maps (Figure 3), he noted that only 10 stations are common despite the fact that the maps report data from a large number of sites. For those 10 common sites, the acidity increased at four (pH went down), decreased at two and remained unchanged at four. The difference in the precipitation chemistry for a rural, east central Illinois site between 1954 and 1977 was investigated by Stensland (1977) to ascertain whether or not the precipitation became more acidic and, if so, why. The two data sets were collected from October 26, 1953, to August 12, 1954, and from May 15, 1977 to February 6, 1978. For the 1977 study, an automatic wet/dry collector of the HASL design was used on a 24-hour event basis. The 1977 measured median pH was 4.1, as compared with the calculated median pH of 5.9 for the 1954 data. The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). The comparison yields:

	<u>1954</u>	<u>1977</u>
$\text{SO}_4^{=}$	60	70 $\mu\text{eq/liter}$
NO_3^-	20	30 $\mu\text{eq/liter}$
$\text{Ca}^{++} + \text{Mg}^{++}$	82	10 $\mu\text{eq/liter}$

With these data there can be little question that the samples in 1954 were much more basic than the 1977 samples. Although both $\text{SO}_4^{=}$ and NO_3^- were apparently lower in the 1954 samples, it was the high levels of soil related species, Ca^{++} plus Mg^{++} (the "hardness"), which produced the high pH in 1954. If the Ca^{++} plus Mg^{++} levels in 1954 had been 10 microequivalent per liter as they were in 1977 at the same site, the calculated pH would have been 4.18, i.e., almost identical to the current 1977 measured pH of 4.1.

The possibility exists, as demonstrated by Stensland (1977) that more calcium and magnesium were present in the atmospheric aerosols in 1954 than in 1977 or that the atmospheric particle loading was higher then. To what extent this "local" conclusion can be extended to the northeastern part of the United States is unknown, so are the meteorological factors that might have contributed to the possible higher atmospheric dust loadings.

Interest in acid rain as an atmospheric chemistry, environmental and ecological issue has dramatically increased in the 1970s, with contributions from individual investigators and from research consortia operating mesoscale precipitation chemistry networks.

In an effort to determine background pH values, Cooper (1976) found the normal rainfall pH over Texas to be 6.5 to 6.6, with extreme variations ranging from 5.8 to 7.3. He also found that the pH

decreased as the alkaline CaCO_3 -bearing particulates were removed. Tabatabai and Laflen (1976) found an average pH of 6.2 in Iowa with high sulfate concentrations. Hoeft et al. (1976) found a similar sulfate dominated rain with the same general values of pH for Wisconsin. Feth et al. (1964) was one of the first American researchers to study the pH of snow, reporting a median of approximately 6.0 for stations in California, Utah, Colorado, Oregon, and Arizona.

Even today there is no high density, synoptic coverage of precipitation chemistry in North America, and the lack of historical data on precipitation composition limits the ability to determine anthropogenic effects on the chemical composition of the atmosphere. Currently, programs in Canada and the United States have begun to measure the composition of atmospheric deposition on a long-term basis. These include the Canadian Network for Sampling Precipitation (CANSAP--initiated in 1976), and the United States National Atmospheric Deposition Program (NADP began to collect weekly samples in July 1978), and the United States Multistate Atmospheric Power Production Pollution Study (MAP3S began to collect precipitation on a 24-hour event basis in October 1976).

The quality and quantity of data available today are highly variable. Nevertheless, the general patterns of spatial distribution of acid precipitation--as a consequence of anthropogenic and/or natural changes--are reasonably consistent and clear, providing mounting evidence on changes in the ionic composition of precipitation over the past 30 years.

A unique "quality control" comparison was performed by Pack (1980) comparing the results of two overlapping precipitation collection networks: the eight-site MAP3S and the nine-site Electric Power Research Institute networks. Both networks collected precipitation for individual storms (24-hour "events"). There are differences between the two networks including collectors, operators and analytical laboratory procedures (Battelle Pacific Northwest for MAP3S and Rockwell International for the EPRI data). The comparison period extended from August 1978 through June 1979. Table 8 shows the results for five ions and for two different H^+ determinations.

The two networks produce almost identical averages for $SO_4^{=}$, NO_3^- and NH_4^+ . The largest differences for NH_4^+ is only 7% when the coastal sites are included but only 1% for the set of noncoastal locations. In view of the many variables that might have created differences, agreement to within 10% supports data comparability. However, the Cl^- and Na^+ concentrations show significant differences that are likely due to an as yet unidentified system difference. The behavior of the pH data, expressed as H^+_{field} and H^+_{lab} in Table 8 is intriguing. There are differences between the field pH (measured immediately after collection) and laboratory pH (measured days or weeks later as part of the full chemical analysis) in both networks. Kadlec and Mohnen (1975) first called attention to this now well-established phenomena. Since Pack's (1980) analysis indicated that the two networks produced comparable data for $SO_4^{=}$, NO_3^- , NH_4^+ and H^+_{lab} , the individual 11 month average values can be combined to produce the isopleths in Figure 4 and Figure 5 for $SO_4^{=}$ and NO_3^- , respectively.

TABLE 8

Network Average Ion Concentrations (in micromoles per liter), Network Standard Deviations (SD), and
EPRI/MAP3S Concentration Ratios.

Data Base	SO_4^{2-}	NO_3^-	NH_4^+	Cl^-	Na^+	H^+ (field)	H^+ (lab)	$(H^+_{lab} + NH_4^+)/ (SO_4^{2-} + NO_3^-)$
EPRI network								
All data								
Concentration	29.26	25.50	17.22	11.22	15.85	97.69	61.79	0.98
SD	7.93	6.79	2.90	7.69	6.35	42.02	19.35	
Noncoastal sites*								
Concentration	28.09	25.46	17.27	8.26	14.08			
SD	6.84	7.26	3.10	3.64	3.69			
MAP3S network								
All data								
Concentration	28.13	25.87	16.08	12.10	9.31	72.35	65.68	0.99
SD	3.92	5.06	4.61	12.68	12.18	12.26	11.09	
Noncoastal sites**								
Concentration	29.68	27.12	17.47	5.61	3.25			
SD	3.18	5.18	4.52	1.11	0.87			
Ratio of EPRI to MAP3S data								
All data	1.04	0.99	1.07	0.93	1.70	1.35	0.94	
Noncoastal sites	0.95	0.94	0.99	1.47	4.33			

*Indian River, Delaware excluded

**Lewis, Delaware and Brookhaven, New York excluded (this was done to examine the effect of excluding the majority of any sea-salt contributions).

(from Pack, 1980)

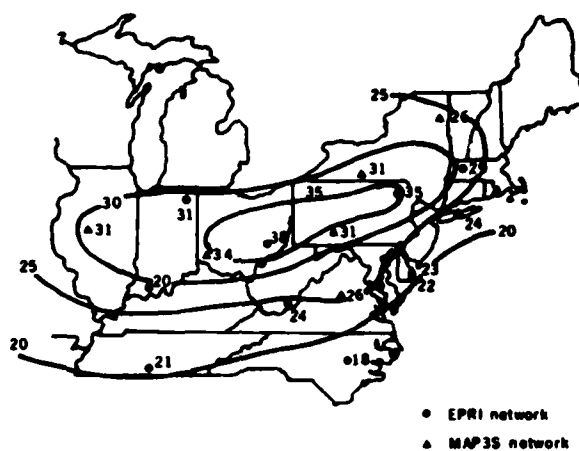


Figure 4. Average SO_4^{2-} concentrations (in micromoles per liter) for the period August 1978 through June 1979. Average concentrations for individual sites are plotted adjacent to the site locations. (from Pack, 1980)

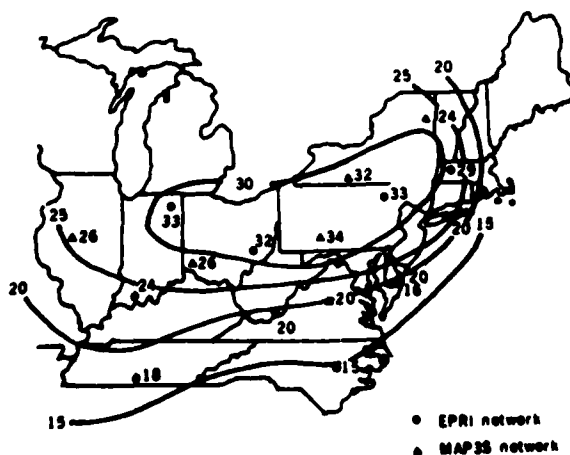


Figure 5. Average NO_3^- concentrations (in micromoles per liter) for the period August 1978 through June 1979. (from Pack, 1980)

There is a definite north-south gradient with the $\text{SO}_4^{=}$ concentrations at the southern edge of the data lower by 30 to 50 percent than the maximum concentrations. An even more marked gradient is discernible for NO_3^- . These data show that selected precipitation chemistry data, carefully collected and rigidly quality controlled can be obtained and intermixed. However, an attempt to incorporate Canadian precipitation chemistry data for the same period of record and the same averaging technique indicated that those data did not compare to either the EPRI or the MAP3S values (Pack, 1980).

These findings also indicate that one cannot compare, without severe limitations, the results of all precipitation analysis including pH obtained by a variety of investigators over a large temporal range and for an almost globally extending area.

With the exception of Houghton (1955), all the studies discussed thus far were made of precipitating clouds with ground based instruments. Oddie (1962) was the first to collect precipitation from an aircraft in a deliberate attempt to prevent below-cloud contamination and/or transformation. He therefore provided the first estimate of the background pH as it exists in clouds as well as the distribution of pH with height. His measurements were made over southern England at varying heights up to 8,500 ft. The pH ranged from 4.4 to 7.2, with a mean of 5.84. One of the most interesting results of the study by Oddie was that the pH for 11 samples taken below 5,000 ft. was 5.4, while the mean pH for 12 samples taken above this height was 6.2, indicating a marked decrease in acidity with height.

An extensive analysis of cloud water pH was performed by Falconer and Falconer (1979). Their results are tabulated in Table 9 and shown in Figure 6. The mean pH for August/September 1977 and 1979 for nonprecipitating clouds was 3.55 and 3.50, respectively, i.e., considerably lower than the pH value for precipitating clouds of 3.96 and 4.01, respectively. The field of cloud chemistry is just emerging in response to the need for a complete atmospheric assessment of all factors affecting acid precipitation.

Several important factors have been discussed in this overview that need to be kept in mind when assessing pH or composition of precipitation. These include knowledge of the exact location where sample was taken and the mode of collection. Figure 7 illustrates the various possibilities. In the past, most precipitation samples were collected over a weekly or monthly period at ground level, i.e., within the planetary boundary layer. Hence, rainout, washout, rain splash and dust settling into the collector influenced the local precipitation quality. The current trend is definitely towards event sampling on a storm-by-storm basis with additional support measurements from above the boundary layer and from within clouds. It is recognized that collecting precipitation on an event basis is essential if the source of the acid precursor material is to be identified through trajectory analysis. In addition to source-receptor studies, efforts to determine the dosage statistics for ecological studies require short sampling periods--even shorter than the now accepted 24-hour periods (Peden and Skowron, 1978).

TABLE 9

Mean hydrogen ion content, H^+ , and pH for precipitating and nonprecipitating clouds at Whiteface Mountain during 1977 and 1979. Variations in H^+ and pH for dewpoint temperatures (T_d) in excess of $60^\circ F$, as measured at the ASRC Field Station at 610 msl, are also shown.

<u>Data</u>	No. of Observations	Mean $[H^+]$ 246 $\mu M L^{-1}$	Mean pH
All records	824		3.61
Precipitating clouds	171	111	3.96
Nonprecipitating clouds	653	282	3.55
Nonprecipitating with $T_d > 60^{\circ}F$	192	478	3.32
Nonprecipitating with $T_d < 60^{\circ}F$	461	200	3.70
1977			
All records	125	243	3.61
Precipitating clouds	43	98	4.01
Nonprecipitating clouds	82	320	3.50
Nonprecipitating clouds with $T_d > 60^{\circ}F$	31	358	3.45
Nonprecipitating clouds with $T_d < 60^{\circ}F$	51	296	3.53
1979			

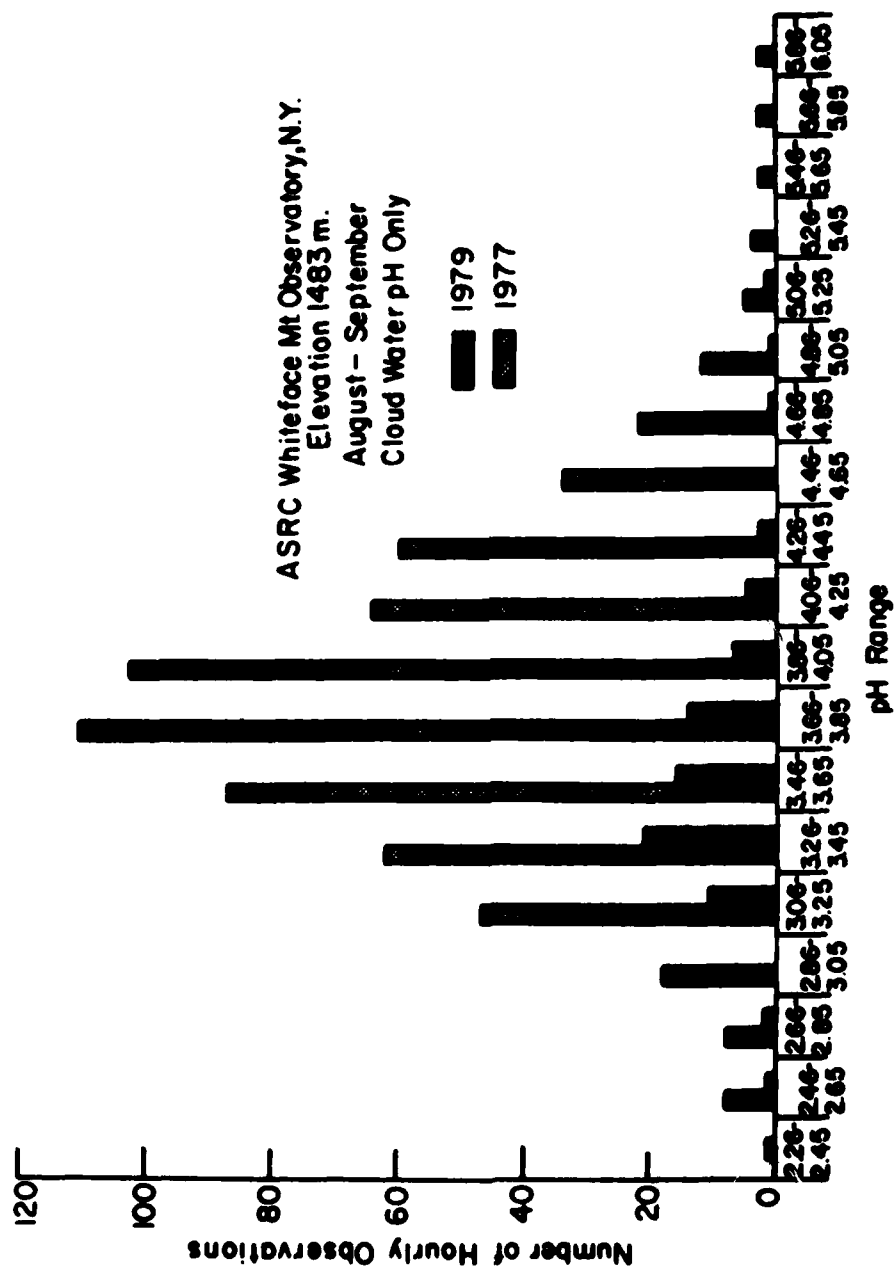


Figure 6. Frequency histograms of hourly pH values for August-September obtained exclusively from non-precipitating cloud events at the Whiteface Mountain Summit Observatory during 1977 and 1979. (Falconer and Kadlecsek, 1980)

PH MEASUREMENTS AND CHARACTERIZATION
OF CLOUDS AND PRECIPITATION ELEMENTS

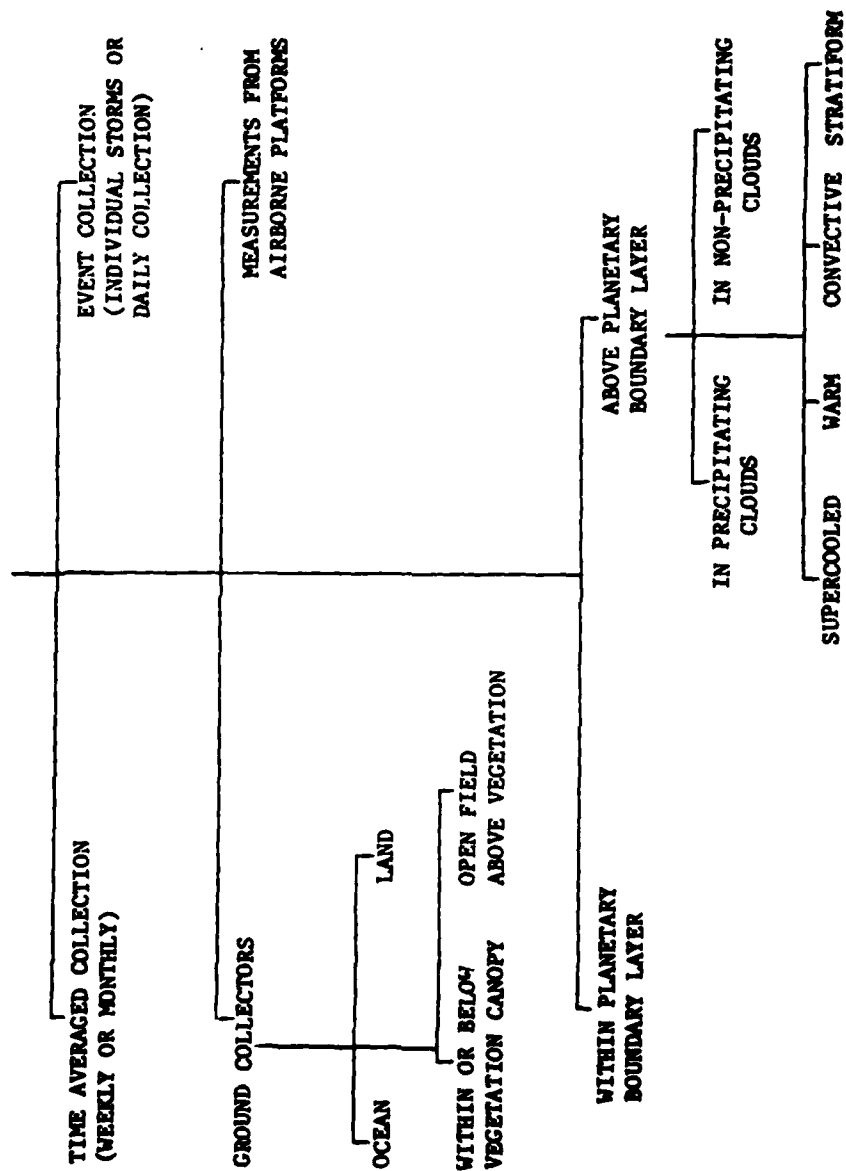


Figure 7. pH measurement classification.

The pH by itself is insufficient to characterize precipitation quality. It is very informative to divide the ionic constituents of precipitation into their categories or components:

- . Soil derived minerals Ca^{++} , Mg^{++} , Fe^{+++} , silicate ions, etc.
- . Sea salt Na^+ , Cl^- , $\text{SO}_4^{=}$ plus small amounts of K^+ , Mg^{++} and Ca^{++}
- . Atmospheric conversion products from sulfur and nitrogen bearing molecules, i.e., $\text{SO}_4^{=}$, NO_3^- , in addition to NH_4^+ and Cl^- (from hydrochloric acid) and, obviously, H^+

Continued and expanded monitoring of precipitation quality is required to evaluate trends and ultimately to provide a high quality, defensible data base for assessment of effects.

2.0 MAP3S PRECIPITATION CHEMISTRY - 1977-1979

2.1 Sampling Network

The dominant source of data is the Multistate Atmospheric Power Production Pollution Study (MAP3S). In this ongoing study, precipitation chemistry data are obtained on an event basis beginning in 1976 for the original MAP3S collection sites of:

- Whiteface Mountain/New York (WFM)
- Ithaca/New York (ITH)
- Pennsylvania State University (PEN)
- University of Virginia (VIR)

In 1977-1978 four more stations were added to the network located at:

- Champaign-Urbana/Illinois (ILL)
- Lewis/Delaware (coastal Site) (LEW)
- Brookhaven, Long Island/ New York (coastal site) (BRO)
- Oxford/Ohio (OXF)

The locations of all MAP3S stations are shown in Figure 8.

The basic precipitation collector used by the MAP3S network during 1977-1979 was a wet deposition-only type designed by Battelle Pacific Northwest Laboratory as shown in Figure 9. This collector allows a relatively large exposed collection area while minimizing splashing and turbulence. An enclosed chamber enables samples to remain refrigerated until their removal for shipment.

Field site operators measure pH, conductivity and sample volume before shipment to Battelle Pacific Northwest Laboratory for complete analysis. Figure 10 describes the chemical species and analysis methods used for identification of various ion species. Field



Figure 8. The MAP3S precipitation chemistry network site array. (MacCracken, 1979)

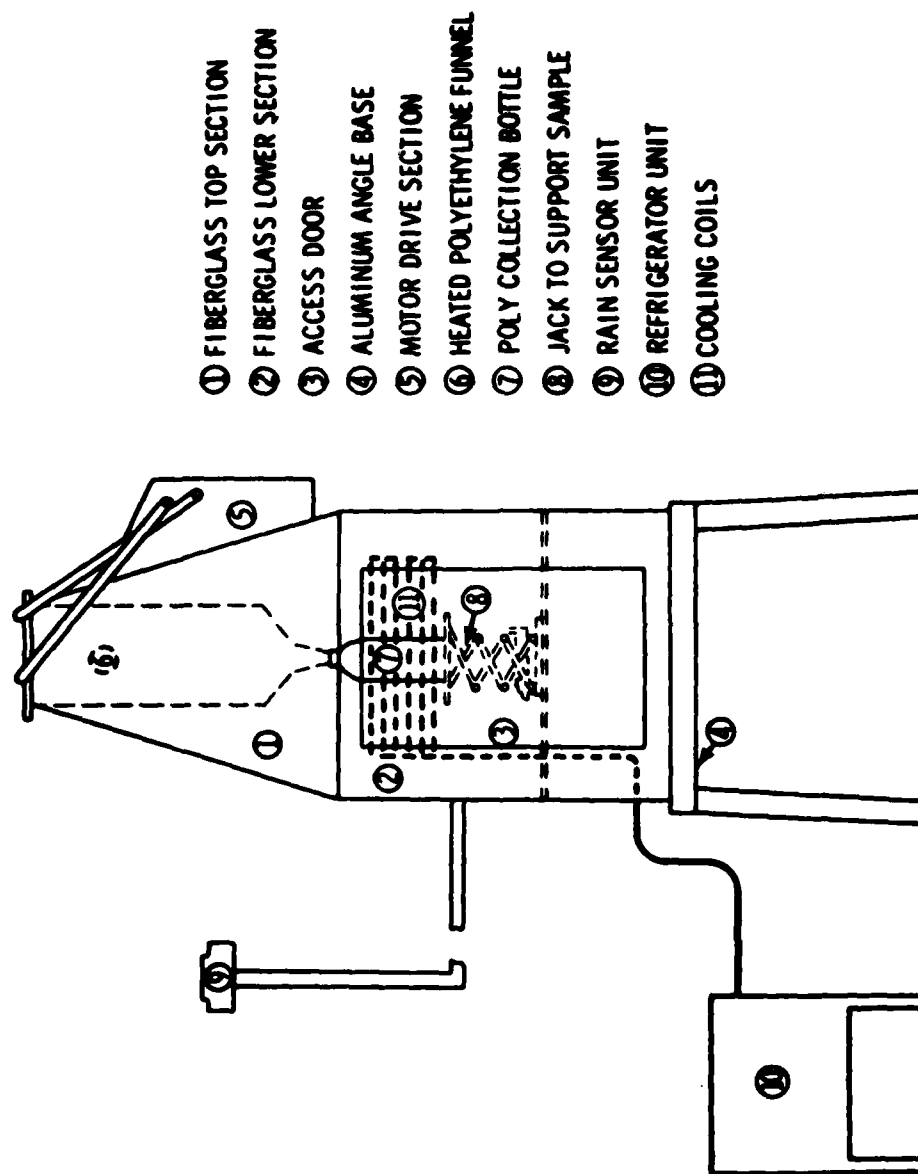


Figure 9. The PNL-designed precipitation collector used by the MAP3S precipitation network. (MacCracken, 1979)

Species	Method*	Instrument	Minimum Limit micromoles/l
H ⁺ (free)	Electrode	Orion 801A, Combination Electrode	-
Conductivity	Bridge	Beckman RC-16C Bridge, Yellow-Springs 3403 Cell	-
SO ₃ ²⁻	AWC	Technicon Auto Analyzer	0.1
SO ₄ ²⁻	IC	Dionex System 10 (Anion)	0.2
NO ₃ ⁻	AWC	Technicon Auto Analyzer	0.05
NO ₂ ⁻	IC	Dionex System 10 (Anion)	0.2
Cl ⁻	IC	Dionex System 10 (Anion)	2.0
PO ₄ ³⁻	IC	Dionex System 10 (Anion)	0.2
NH ₄ ⁺	IC	Dionex System 10 (Cation)	0.6
Na ⁺	IC	Dionex System 10 (Cation)	0.4
K ⁺	IC	Dionex System 10 (Cation)	0.25
Ca ⁺⁺	AA	Perkin-Elmer 306	0.25
Mg ⁺⁺	AA	Perkin-Elmer 306	0.4

* AWC = Automated Wet Chemistry; IC = Ion Chromatography; AA = Atomic Absorption Spectrophotometry.

Figure 10. Chemical species and analysis methods.
(MacCracken, 1979)

determinations of pH and hydrogen ion concentration are annotated as $F[H^+]$ while $L[H^+]$ delineates laboratory measurements.

2.2 Average Event Concentration and Deposition

It is desirable first to obtain an overview of precipitation chemistry in terms of average concentration and deposition at various sites before conducting detailed case studies. Since concentration is greatly influenced by the amount of event sample volume, a weighted scheme was used to calculate precipitation weighted means for ions at the four original sites for 1977-1979. The weighted concentration values, \bar{C} , were expressed according to the formula

$$\bar{C} = \frac{\sum_{i=1}^N P_i C_i}{\sum_{i=1}^N P_i},$$

where P_i = event sample volume

C_i = event ion concentration

N = number of observations.

Table 10 shows the precipitation weighted concentrations, as well as the overall mean for $SO_4^{=}$, NO_3^- , H^+ and NH_4^+ for each year of the three year period of study. Ithaca and Penn State display a generally higher concentration of pollutant-related ions in precipitation followed by Virginia and Whiteface Mountain. The cation-to-anion ratio near unity indicates an approximate balance of the four ionic species that seem to dominate the precipitation chemistry in the northeastern United States.

TABLE 10

CONCENTRATION [$\mu\text{mole/liter}$]

	Total Sample Volume	Intensity weighted SO_4^{2-} Mean		Intensity weighted NO_3^- Mean		Intensity weighted LiH^+ Mean		Intensity weighted NH_4^+ Mean	
		($\mu\text{mole/liter}$)	No. of significant events/total events	($\mu\text{mole/liter}$)	No. of significant events/total events	($\mu\text{mole/liter}$)	No. of significant events/total events	($\mu\text{mole/liter}$)	No. of significant events/total events
MASS	1977 52674	21.45	17/82	22.48	9/83	42.39	17/71	10.36	13/73
	1978 34364	28.32	11/55	25.08	12/55	58.79	11/54	16.67	12/55
	1979 52214	18.86	9/45	18.13	12/45	44.97	10/45	10.13	5/45
ITHACA	1977 36850	30.91	4/44	28.65	6/44	55.21	6/30	12.97	8/42
	1978 36422	32.93	15/59	30.40	10/60	66.32	12/56	15.22	9/57
	1979 47275	27.27	11/61	23.92	13/60	67.84	8/59	14.69	9/60
PENN STATE	1977 44394	31.00	19/83	30.55	17/83	59.22	8/51	13.83	14/74
	1978 42621	29.30	17/71	29.34	11/71	64.74	14/58	12.98	8/70
	1979 58879	27.93	10/77	27.01	13/77	63.41	14/74	15.85	10/76
VIRGINIA	1977 25742	34.57	9/48	27.53	7/48	60.04	5/35	14.31	8/45
	1978 41891	28.29	9/54	24.74	3/54	66.68	3/50	12.28	5/54
	21979 38906	24.08	10/53	21.10	8/52	63.70	8/51	11.08	5/52
Intensity weighted averages for 1977-1979 period									
MASS	46317	22.88		21.90		48.72		12.39	1.11
ITHACA	40182	30.37		27.66		63.12		14.29	1.14
PENN STATE	48631	29.41		28.97		62.46		14.22	1.14
VIRGINIA	35513	28.98		24.46		63.47		12.54	1.08

¹A significant event is defined as one whose value is greater than the intensity weighted mean plus one standard deviation.
²Virginia 1979 was corrected for events missed between 10 October and 26 November.

The number of total events as well as "significant" events is also included in Table 10. The concentrations and percent contribution to the total amount of wet deposition of the "significant" events is of particular interest and will be addressed later. A "significant" event was defined as one whose values were greater than the mean plus one standard deviation. Frequency plots of both concentration and deposition were found to be strongly log-normal in their distribution.

Wet deposition is a function of concentration and precipitation amount. Event deposition measurements can therefore encompass a wide range of values. These event deposition values are needed to assess long-term considerations of pollutant deposition. Table 11 depicts the arithmetic wet deposition mean for $\text{SO}_4^{=}$, NO_3^- , H^+ and NH_4^+ during 1977-1979 for the four original MAP3S sites. Significant events, three-year means, and cation-to-anion ratios are also presented. A pattern similar to that of concentration emerges whereby Ithaca and Penn State have the highest average deposition followed by Virginia and Whiteface Mountain.

2.3 Event and Monthly Deposition

Ionic concentration and wet deposition for some constituents is known to be seasonal in nature. In order to visualize these variations from the average values of Table 11, event and monthly deposition for Whiteface Mountain for 1977-1979 is plotted in Figures 11-13.

Precipitation and NO_3^- deposition demonstrates no identifiable sinusoidal or periodic oscillation between the seasons or years. However, H^+ , $\text{SO}_4^{=}$, NH_4^+ and the soil components $\text{Ca}^{++} + \text{Mg}^{++}$ have a

TABLE 11

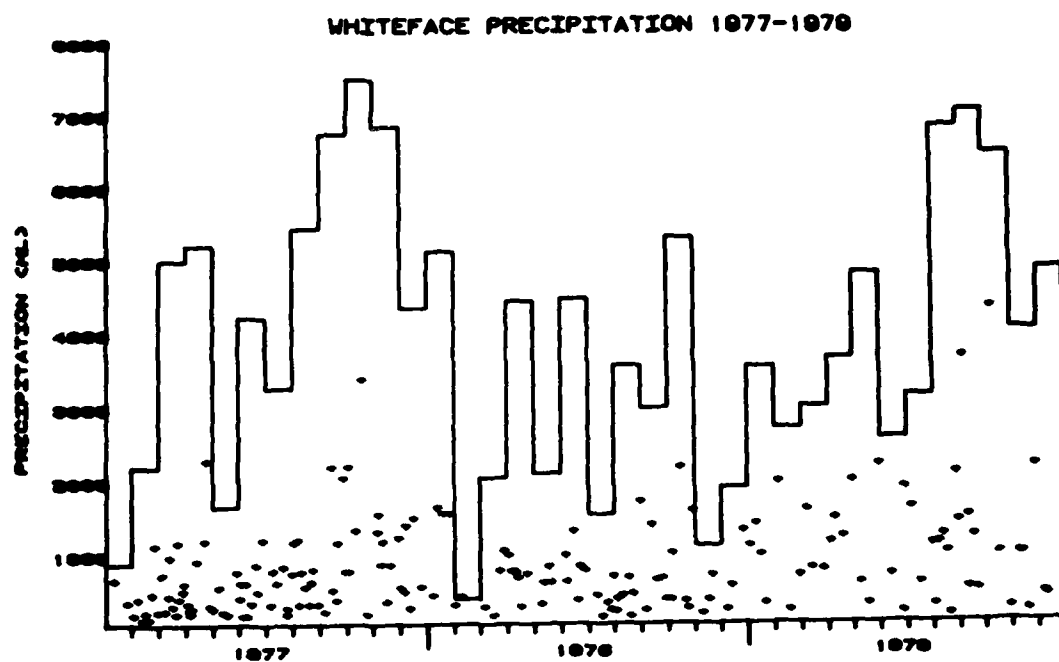
Mean Deposition ($\mu\text{g}/\text{m}^2$) and microequivalent/ m^2

	SO_4^{2-}			NO_3^-			$\text{L}^+(\text{H}^+)$			NH_4^+		
	$\mu\text{g}/\text{m}^2$	Significant Events/ Total Events	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	Significant Events/ Total Events	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	Significant Events/ Total Events	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	Significant Events/ Total Events	$\mu\text{g}/\text{m}^2$
WPN	27	563	13/82	18	291	7/83	0.64	640	9/71	2.8	152	9/73
	35	723	4/55	20	320	7/55	0.76	763	5/54	3.8	213	6/55
	42	884	4/45	26	420	7/45	1.05	1047	6/45	4.3	237	6/45
ITHACA	51	1057	6/44	30	490	4/44	1.38	1383	5/30	4.2	232	6/42
	40	830	8/59	23	376	7/60	0.88	880	8/56	3.6	198	8/57
	40	830	6/61	22	356	8/60	1.06	1058	7/59	4.1	228	5/60
PENN STATE	32	677	13/83	21	333	11/83	1.05	1052	9/51	3.1	169	6/74
	35	718	10/71	22	366	9/71	0.97	970	7/58	2.8	155	5/70
	41	862	9/77	26	415	8/77	1.02	1018	11/74	4.5	248	7/76
VIRGINIA	36	757	3/48	19	301	5/48	0.91	901	4/35	3.0	167	2/45
	42	881	11/54	24	380	7/54	1.11	1113	10/50	3.5	191	9/54
	35	731	5/53	20	319	7/53	1.00	1004	5/51	3.1	171	7/52
$C = (\text{SO}_4^{2-} + \text{NO}_3^-) \quad A = (\text{L}^+(\text{H}^+) + \text{NH}_4^+) \quad C/A \text{ (cations/anions)}$												
WPN	52674	854	3 yr. mean	792	3 yr. mean	1.08	3 yr. mean	1.08	1.05			
	34364	1043	1070	967	1015	1.08		1.06				
	52214	1304	1284	1284								
ITHACA	36850	1547	3 yr. mean	1615	3 yr. mean	0.96	3 yr. mean	0.96	0.99			
	36422	1206	1313	1087	1321	1.12		1.12				
	47275	1186	1186	1286		0.92		0.92				
PENN STATE	44394	1010	3 yr. mean	1221	3 yr. mean	0.83	3 yr. mean	0.83	0.93			
	42621	1084	1124	1125	1203	0.96		0.96				
	58933	1277	1277	1266		1.01		1.01				
VIRGINIA	25742	1058	3 yr. mean	1068	3 yr. mean	0.99	3 yr. mean	0.99	0.95			
	41841	1262	1123	1304	1182	0.97		0.97				
	38906	1050	1050	1175		0.95		0.95				

1 A significant event is defined as one whose values is greater than the mean plus one standard deviation.

2 Virginia 1979 was corrected for events missed between 10 October and 26 November.

a)



b)

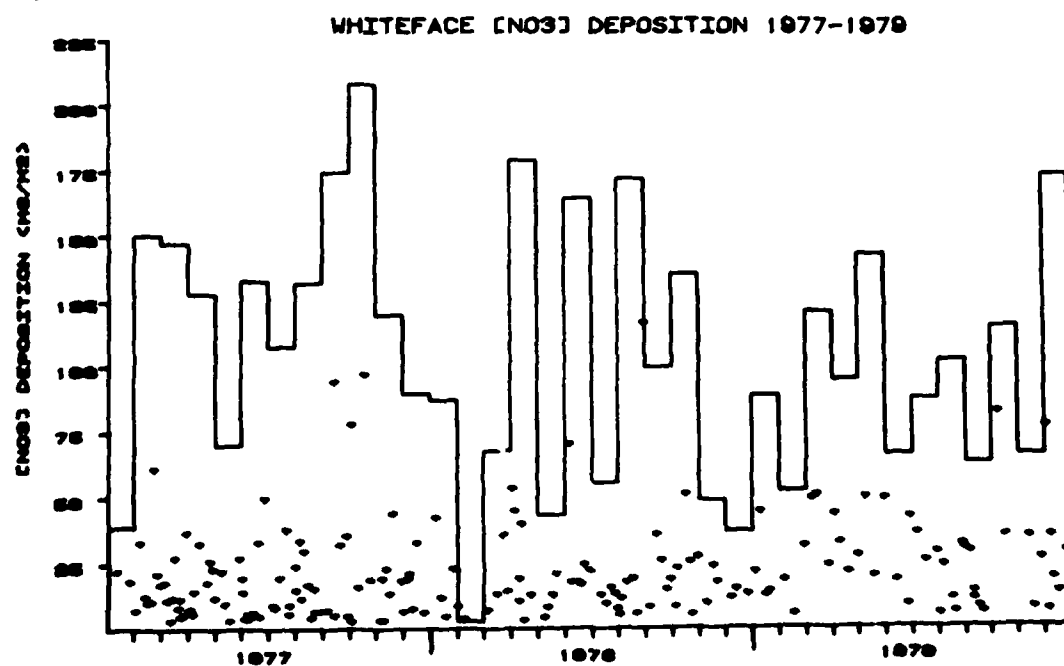


Figure 11. a) Precipitation events and monthly totals, and
b) Event and monthly nitrate deposition for Whiteface,
1977-1979.

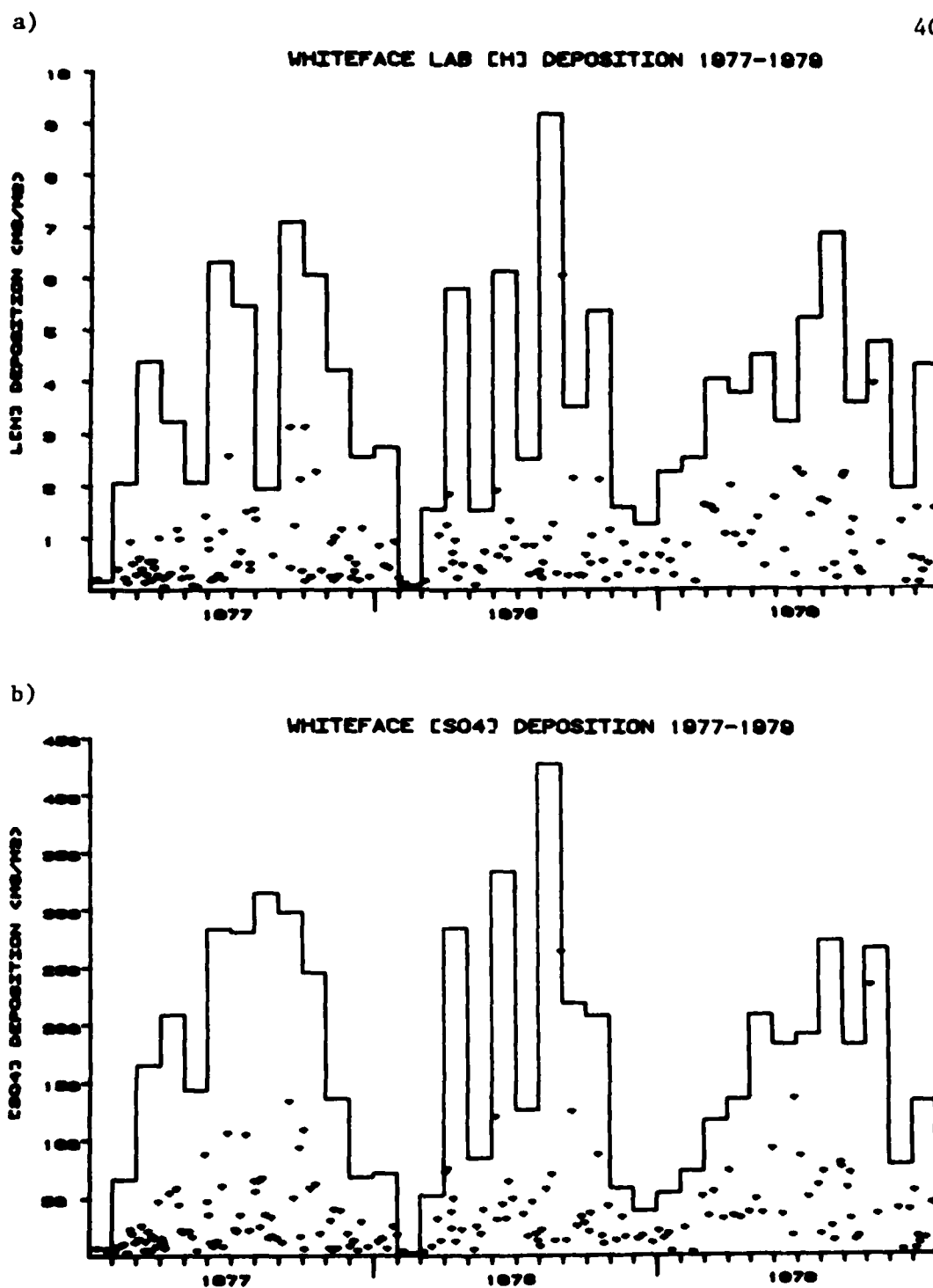


Figure 12. a) Free hydrogen ion event and monthly deposition, and b) Sulfate event and monthly deposition for Whiteface, 1977-1979.

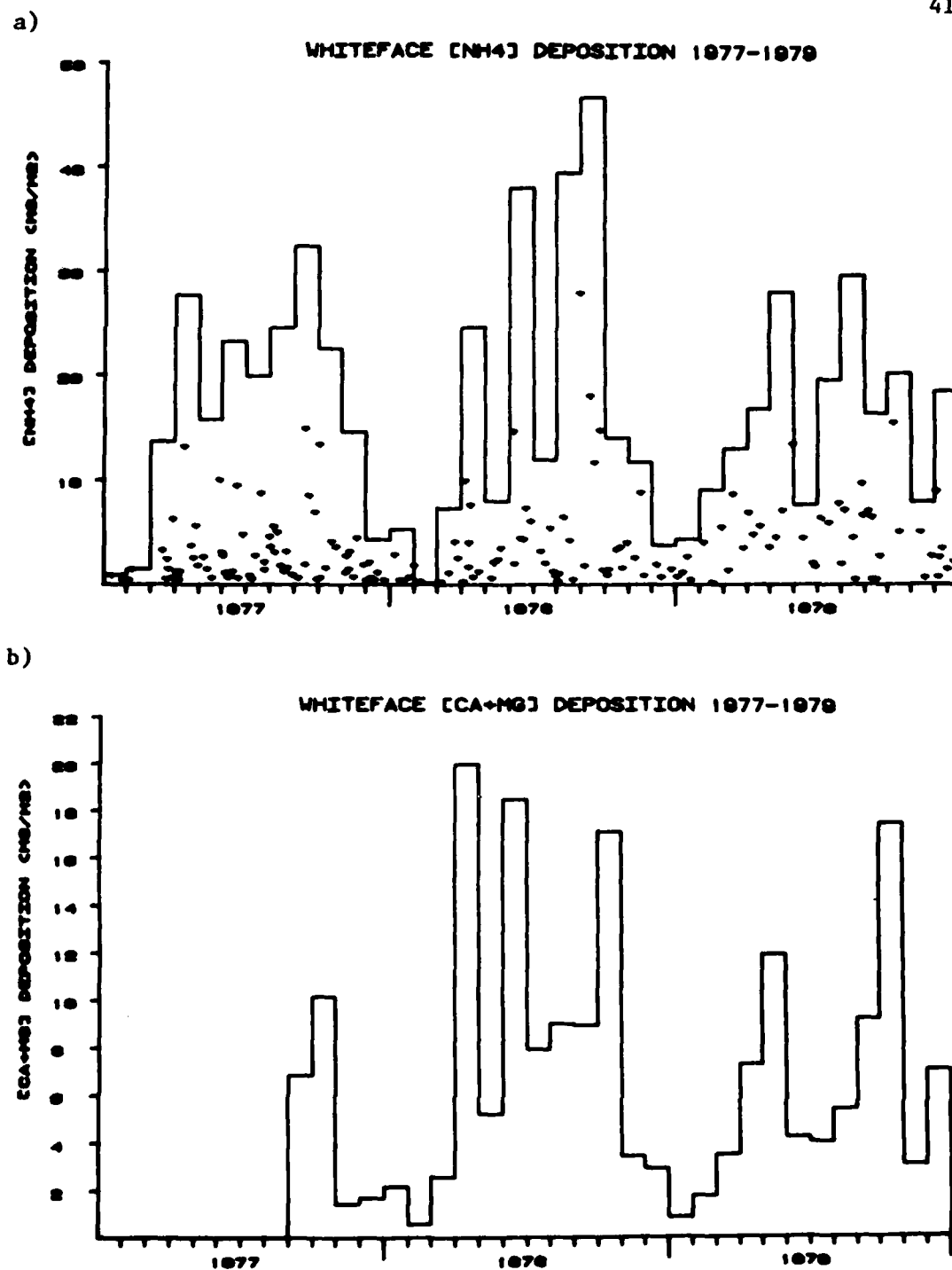


Figure 13. a) Ammonium event and monthly deposition, and b) Soil component ($\text{Ca}^{++} + \text{Mg}^{++}$) monthly deposition for Whiteface, 1977-1979.

definite summer maximum and winter minimum. The enhanced overall transformation of SO_2 to $\text{SO}_4^{=}$, due to the increase in solar radiation and other yet to be determined factors, is a likely reason for $\text{SO}_4^{=}$ being the dominant ion in summer precipitation in the northeastern United States, and therefore becomes the forcing function in the free hydrogen ion concentration and deposition. Values of the soil components $[\text{Ca}^{++} + \text{Mg}^{++}]$ are not plotted for the first part of 1977, since these ions were not part of the routine analysis prior to August 1977.

2.4 Total Wet Deposition

In order to gain insight into the climatology of ion deposition, total wet deposition of the dominant ions was examined for various stations for one- and three-year periods. The stations chosen were again Whiteface Mountain, Ithaca, Penn State, and Virginia. Table 12 presents the yearly totals for deposition of the dominant ions expressed in mg/m^2 and microequivalents/ m^2 , along with the anion/cation ratio for 1977-79.

This table illustrates the variability in wet deposition on both the temporal and spatial scale. Spatial variability is difficult to interpret since the degree of coherency between stations is not usually proven. Pack (1980) showed independent stations could be used to develop regional patterns if one-year averages are used. In this context, spatial variability is best discussed for long-term averages or totals of one to three years similar to those of Table 12.

TABLE 12

		Total Deposition [mg/m ²] and [μeq/m ²]									
	Sample Volume ml	[SO ₄ ^{m-}]	[NO ₃ ⁻]	[H ⁺] _L	[NH ₄ ⁺]	[SO ₄] ⁻ + [NO ₃] ⁻					
		mg/m ² μeq/m ²	mg/m ² μeq/m ²	mg/m ² μeq/m ²	mg/m ² μeq/m ²	mg/m ² μeq/m ²	[H] + [NH ₄]				
WPH	1977	52674	2333	48604	1495	24111	46.5	46500	201	11123	1.26
	1978	34364	1908	39750	1091	17595	41.2	41200	211	11676	1.08
	1979	52214	1908	39750	1346	21708	47.1	47100	192	10625	1.06
ITHACA	1977	36850	2233	46521	1336	21547	41.5	41500	176	9739	1.33
	1978	36422	2351	48979	1401	22595	49.3	49300	204	11289	1.18
	1979	47275	2429	50604	1346	21708	62.0	62000	248	13723	0.95
PENN STATE	1977	44394	2698	56208	1716	27676	53.7	53700	226	12506	1.27
	1978	42621	2448	51000	1583	25531	56.3	56300	196	10845	1.14
	1979	58933	3188	66416	1983	31982	75.0	75000	341	18870	1.05
VIRGINIA	1977	25742	1744	36333	897	14467	31.5	31500	136	7526	1.30
	1978	41841	2284	47583	1273	20531	55.7	55700	186	10293	1.03
	1979	38906	1620	33750	913	14725	44.0	44000	140	7747	0.94

The totals given in Table 12 are the total wet deposition values for the various ions as measured by the MAP3S sites. The amount of sample volume reported will be influenced by the efficiency of the precipitation collector, the care in sample handling, and the percentage of events actually sampled. These considerations become important when attempting to conduct inter-site or regional total deposition comparisons. When compared with the published precipitation measurements of the National Climatic Center (NCC) and with comparable measurements at the Atmospheric Sciences Research Center's Whiteface Mountain station, the calculated precipitation amounts from the MAP3S network are somewhat low. The ratio of these two different precipitation estimates (MAP3S versus NCC and Whiteface Mountain) has been determined for Whiteface Mountain, Penn State, Ithaca, and Virginia to be of the order of 0.96, 0.93, 0.85 and 0.61, respectively. Therefore, reported MAP3S measurements of total wet deposition are approximately underestimated by 4%, 7%, 15% and 39%, respectively, for the above four stations.

2.5 Cumulative Deposition

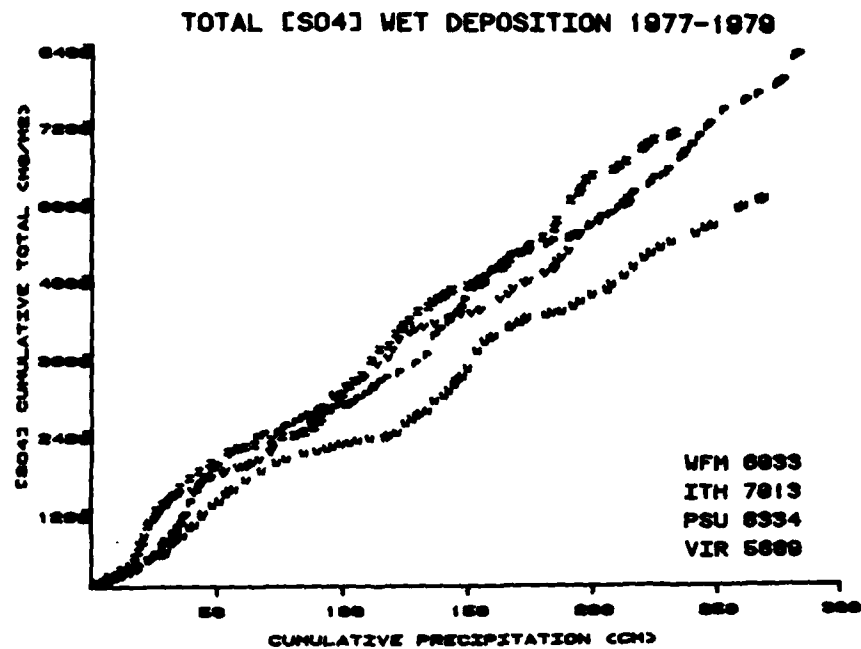
Because of inherent time and space averaging in accumulated wet deposition, this parameter acquires regional significance. Data of the MAP3S network offers a unique chance to examine the cumulative deposition of major ions in precipitation over a three-year period and to develop statistical relationships between wet deposition and various meteorological parameters. The four original inland MAP3S stations are considered to be representative of the northeastern region.

To describe the total measured wet deposition at each site, the cumulative ion depositions for $\text{SO}_4^{=}$, NO_3^{-} , H^{+} , and NH_4^{+} were plotted as a function of cumulative precipitation measured at each site. These plots are shown in Figures 14 and 15. For clarity, only every other event represented by a symbol was plotted. This diagram offers the advantage of relating the total amount of pollution related ion deposition to a given amount of total precipitation integrated over relatively long time periods. Any change in accumulation such as during the periodic oscillations of $\text{SO}_4^{=}$, and to a lesser extent H^{+} and NH_4^{+} , are thus clearly discernible. A cumulative plot of $\text{SO}_4^{=}$ wet deposition as a function of time rather than precipitation shows this accumulation to be due to the well-known summer sulfate concentration maximum and not to enhanced precipitation. The strong anion NO_3^{-} cumulative wet deposition pattern in Figure 14b suggests a rather uniform concentration and subsequent deposition of NO_3^{-} throughout the three-year period.

Linear regression techniques were applied to the cumulative data and the resulting parameters are shown in Table 13. (The model chosen required the regression line to pass through the origin.) Even though event and seasonal fluctuations in ionic concentration are not directly considered in these equations, this method still offers a viable means to estimate total wet deposition of various ions if the time period during which precipitation events are included is sufficiently long. Obviously, deposition estimates for time scales of the order of days or weeks may not produce results compatible with those based on the above procedures.

a)

46



b)

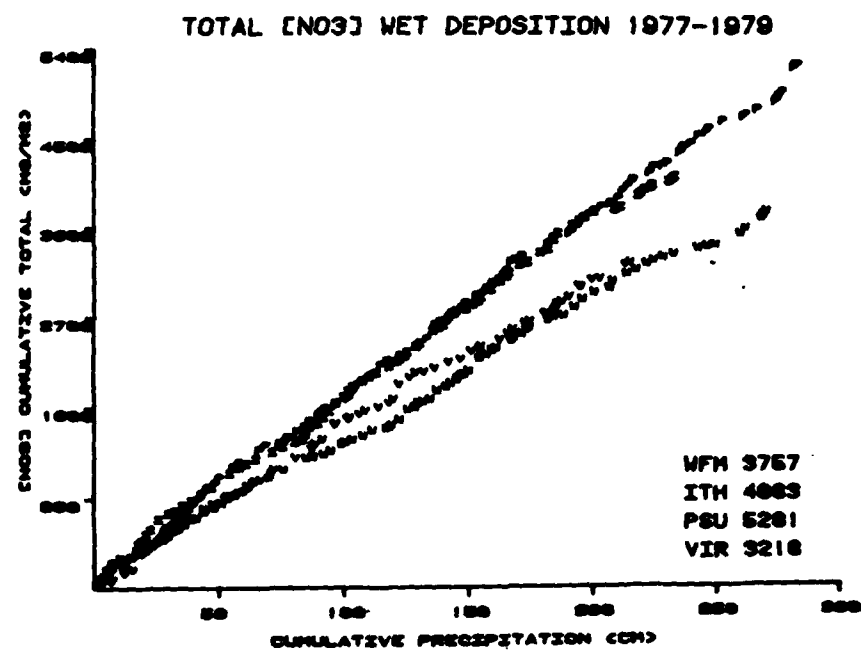
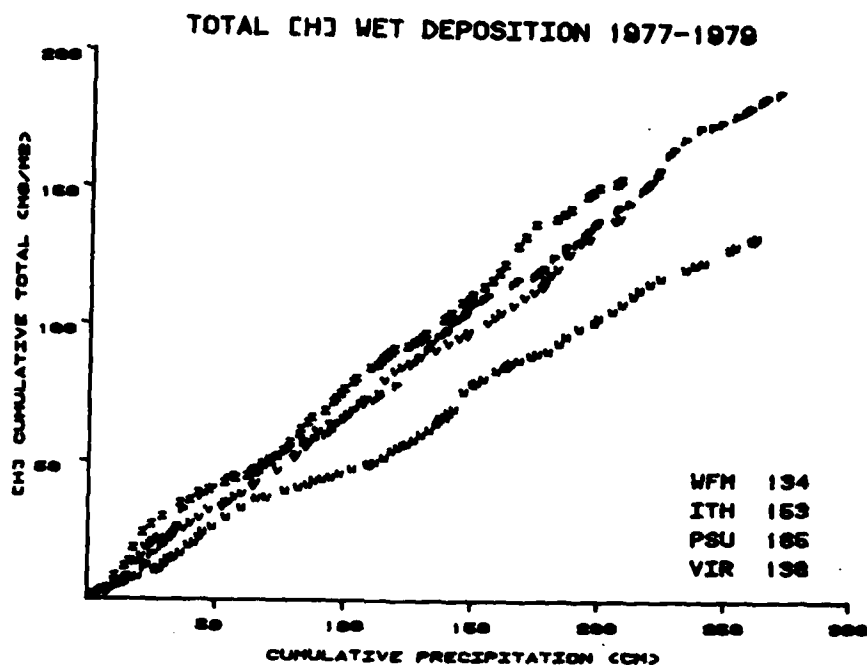


Figure 14. Incremental cumulative totals of wet deposition vs. cumulative precipitation during 1977-1979 for
a) SO_4^{2-} and b) NO_3^- .

a)



b)

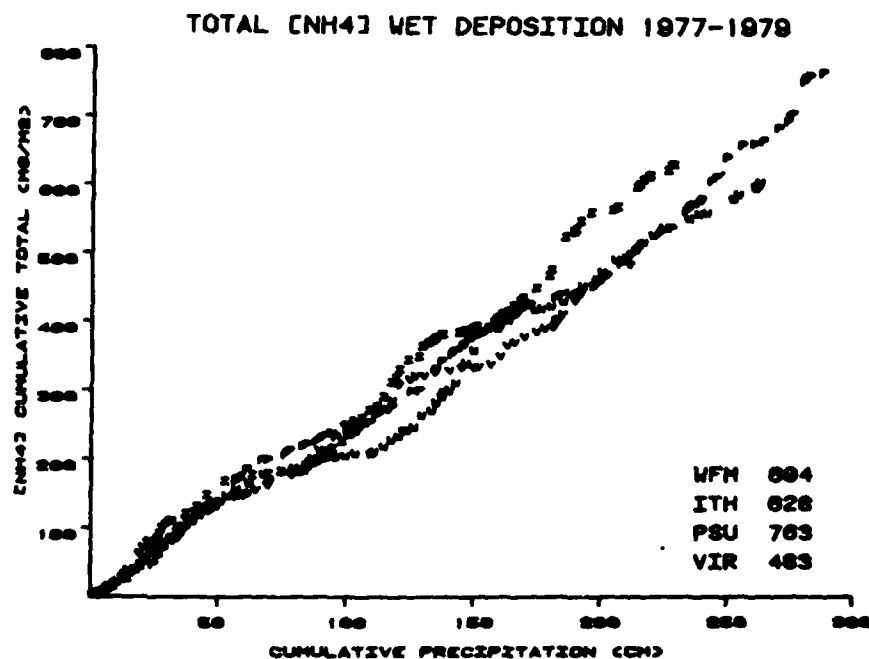


Figure 15. Incremental cumulative totals of wet deposition vs. cumulative precipitation during 1977-1979 for
a) H⁺ and b) NH₄⁺

TABLE 13

Wet Deposition Regression Equations

$$D = \beta P$$

where D = cumulative wet deposition (mg/m²)

P = cumulative precipitation (cm)

β = regression slope

Station	Ion	β	Standard Error of Estimate for β	Non-Cumulative Variance ($\hat{\sigma}^2$)
Whiteface Mountain	SO ₄ ⁻	22.40	1.06	841.77
	NO ₃ ⁻	14.24	0.58	252.24
	H ⁺	0.50	0.02	0.38
	NH ₄ ⁺	2.29	0.14	14.20
Penn State	SO ₄ ⁻	28.63	1.17	1093.42
	NO ₃ ⁻	18.47	0.66	352.32
	H ⁺	0.69	0.03	0.51
	NH ₄ ⁺	2.47	0.15	17.95
Ithaca	SO ₄ ⁻	30.80	1.52	1394.67
	NO ₃ ⁻	18.41	0.71	304.10
	H ⁺	0.75	0.03	0.62
	NH ₄ ⁺	2.67	0.19	20.29
Virginia	SO ₄ ⁻	28.18	1.37	1210.16
	NO ₃ ⁻	15.48	0.72	330.63
	H ⁺	0.66	0.03	0.56
	NH ₄ ⁺	2.29	0.14	11.79

Normal procedures for calculation of the standard errors of estimate were found to be inadequate due to autocorrelation of the resultant residuals. A model utilizing non-cumulative data was utilized to account for the inherent problems of correlation. If

$$Y_i = \beta X_i + E_i$$

is the deposition equation for the non-cumulative data where Y_i = event deposition (mg/m²) and X_i = event precipitation (cm), then the estimated variance of the non-cumulative data can be written as

$$\hat{\sigma}^2 = \frac{1}{N-1} \left\{ \sum_{i=1}^N Y_i^2 - \frac{(\sum_{i=1}^N X_i Y_i)^2}{\sum_{i=1}^N X_i^2} \right\}$$

where N = number of observations. The slope, β , can be expressed as

$$\beta = \frac{\sum_{i=1}^N X_i Y_i}{\sum_{i=1}^N X_i^2}$$

The cumulative model may therefore be written as

$$Z_j = \beta U_j + \epsilon_j$$

where

$$Z_j = \sum_{i=1}^N Y_i, U = \sum_{i=1}^N X_i, \text{ and } \epsilon_j = \sum_{i=1}^N E_i.$$

The standard error of estimate for the cumulative data can then be expressed as

$$\left(\frac{\hat{\sigma}^2 U_j^2}{\sum_{i=1}^N X_i^2} \right)^{1/2}.$$

This procedure applied to Whiteface Mountain, which had a total of 273 cm of precipitation at the end of the three-year period, yielded total depositions in mg/m^2 of (6115 ± 324) , (3887 ± 178) , (136 ± 7) , and (625 ± 41) for $\text{SO}_4^{=}$, NO_3^- , H^+ , and NH_4^+ , respectively.

Time series analysis would be needed to account completely for the periodic oscillations in cumulative deposition relating to summertime maximum in concentration. However, such a treatment would require a data base of the order of 5-10 years, which is unavailable today. Therefore, a simple linear model was developed here to describe the three-year MAP3S data.

The slope of the accumulated ion deposition, or β parameter, can be used to characterize regional deposition patterns since normalization to unit amounts of precipitation allows for inter-site comparisons. This concept will be extensively discussed in a later chapter.

2.6 Ion Balances

To insure that an ionic balance was maintained between the major ions $\text{SO}_4^{=}$, NO_3^- , H^+ and NH_4^+ throughout the three-year period, ions or pairs of ions were analyzed for correlation or degree of association.

Figure 16 shows the balance between the four dominant ions, $\text{SO}_4^{=}$, NO_3^- , H^+ , and NH_4^+ . The linear correlation coefficient of 0.95 for Whiteface Mountain indicates that a significant portion of the sulfate and nitrate could exist in the form of sulfuric and nitric acid and the appropriate ammonium salts.

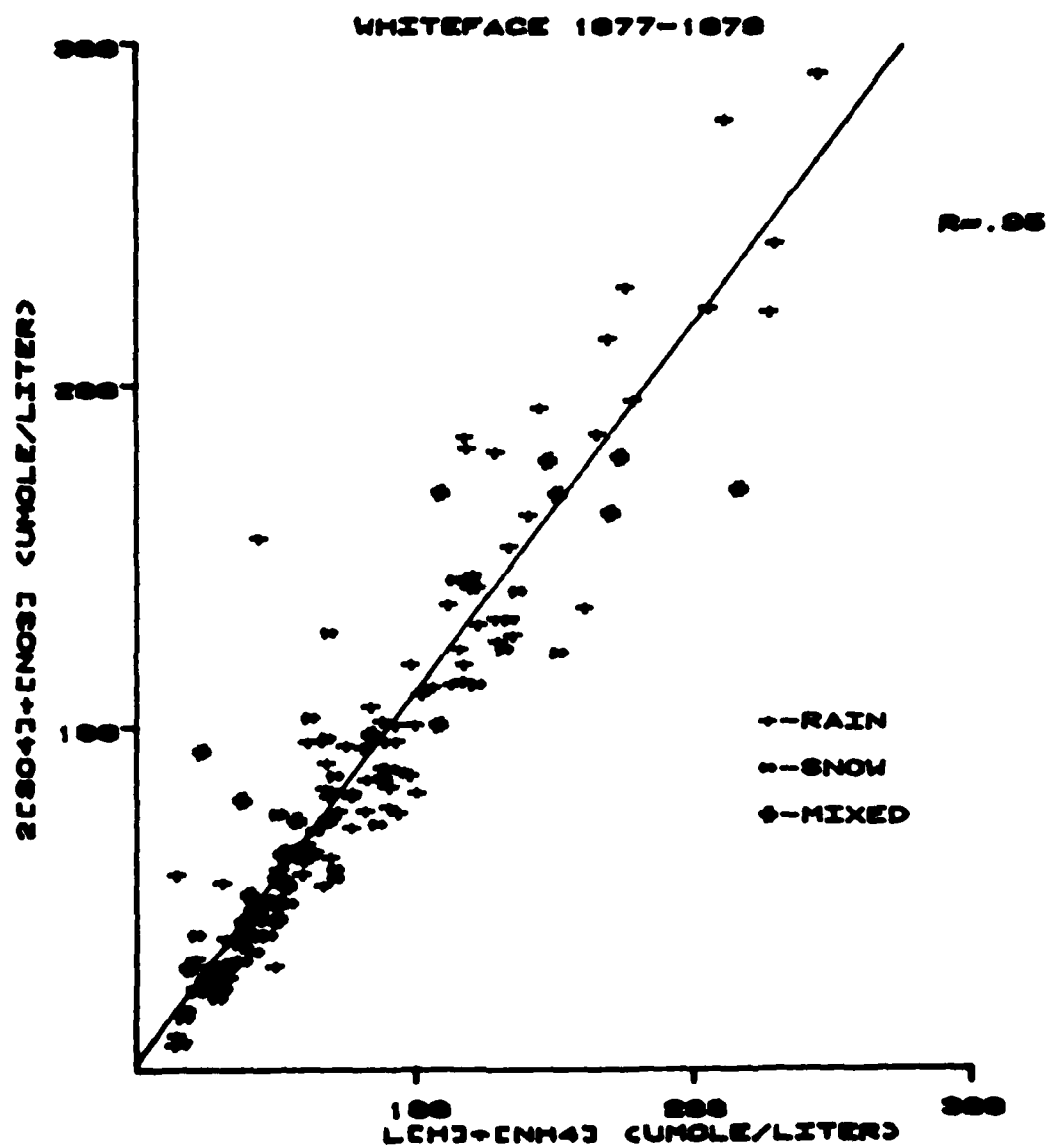


Figure 16. Hydrogen + Ammonium vs. 2(Sulfate) + Nitrate for Whiteface, 1977-1979.

The linear correlation can further be improved by removing the soil components, indicated by Ca^{++} and Mg^{++} , from the cation summation as shown in Figure 17. The correlation of 0.98 suggests an extremely good ion balance exists whenever boundary layer influences such as soil components can be reduced.

This procedure can also be used to determine the degree of dependency of the pH, or H^+ , upon the other three major constituents. Figures 18 through 20 show this degree of association between H^+ and $\text{SO}_4^{=}$, NO_3^- , and NH_4^+ , respectively. The concentration of H^+ in precipitation is determined primarily by $\text{SO}_4^{=}$, to a lesser extent NO_3^- , and finally NH_4^+ . This conclusion applies to all types of precipitation for all three analyses.

Comparisons of precipitation volume and ion concentration for singular events indicate the existence of an inverse relationship between the two parameters. Figures 21 through 24 illustrate this inverse association, or diluting effect, of large amounts of precipitation upon ionic concentration. Since NO_3^- normally exists in the form of vapor while $\text{SO}_4^{=}$ is considered to be an aerosol, the removal rates by precipitation should be somewhat different. One could infer from Figure 22 a more rapid removal of vaporous NO_3^- than of the aerosol $\text{SO}_4^{=}$ shown in Figure 21. It appears that most of the available NO_3^- is already removed by small precipitation volumes with relatively small contributions from additional precipitation.

The distribution of $\text{SO}_4^{=}$ with sample volume indicates a much more gradual removal for all forms of precipitation with a more effective removal of $\text{SO}_4^{=}$ by snow and mixed precipitation.

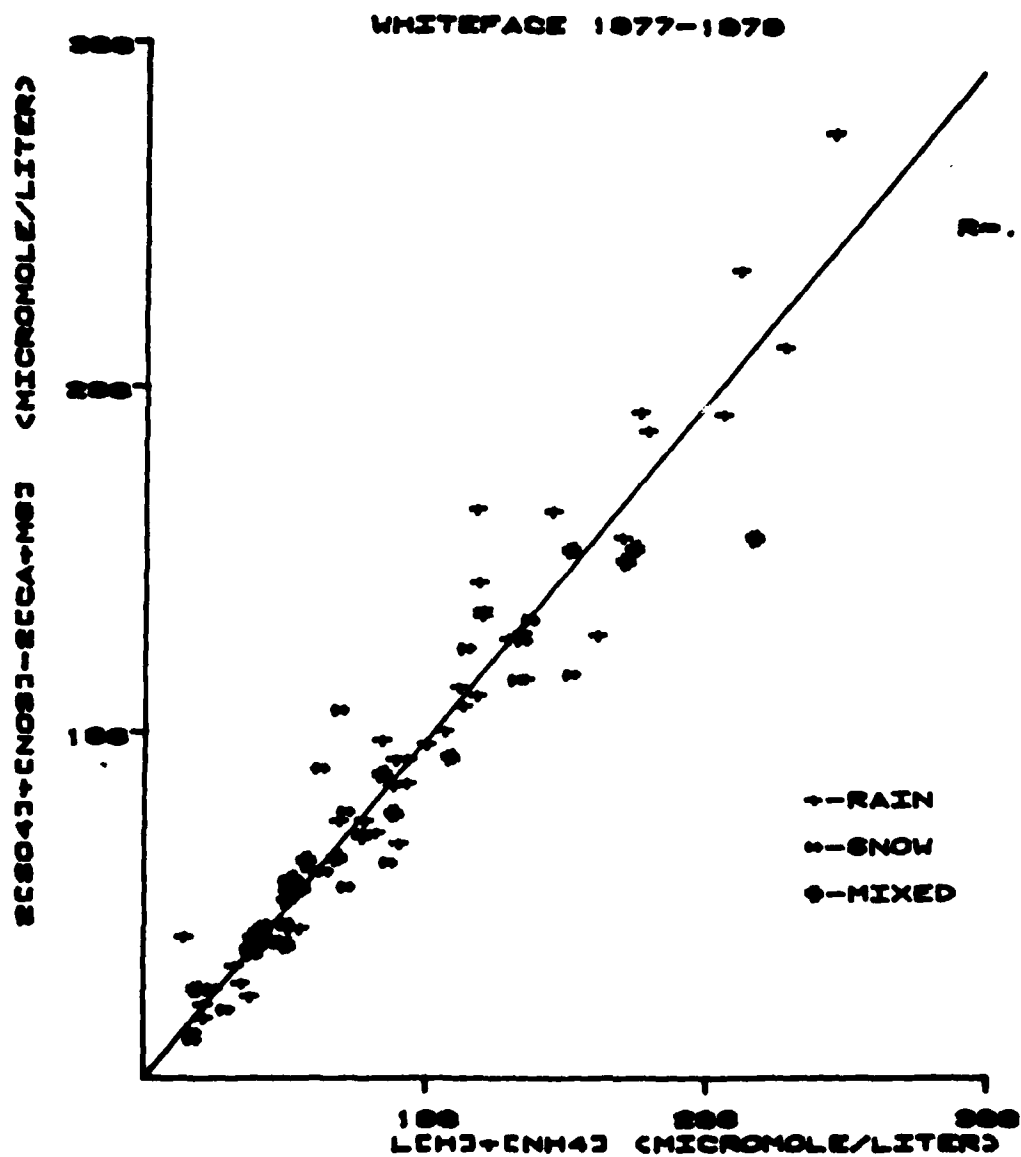


Figure 17. Hydrogen + Ammonium vs. 2(Sulfate) + Nitrate - 2(Soil Components) for Whiteface, 1977-1979.

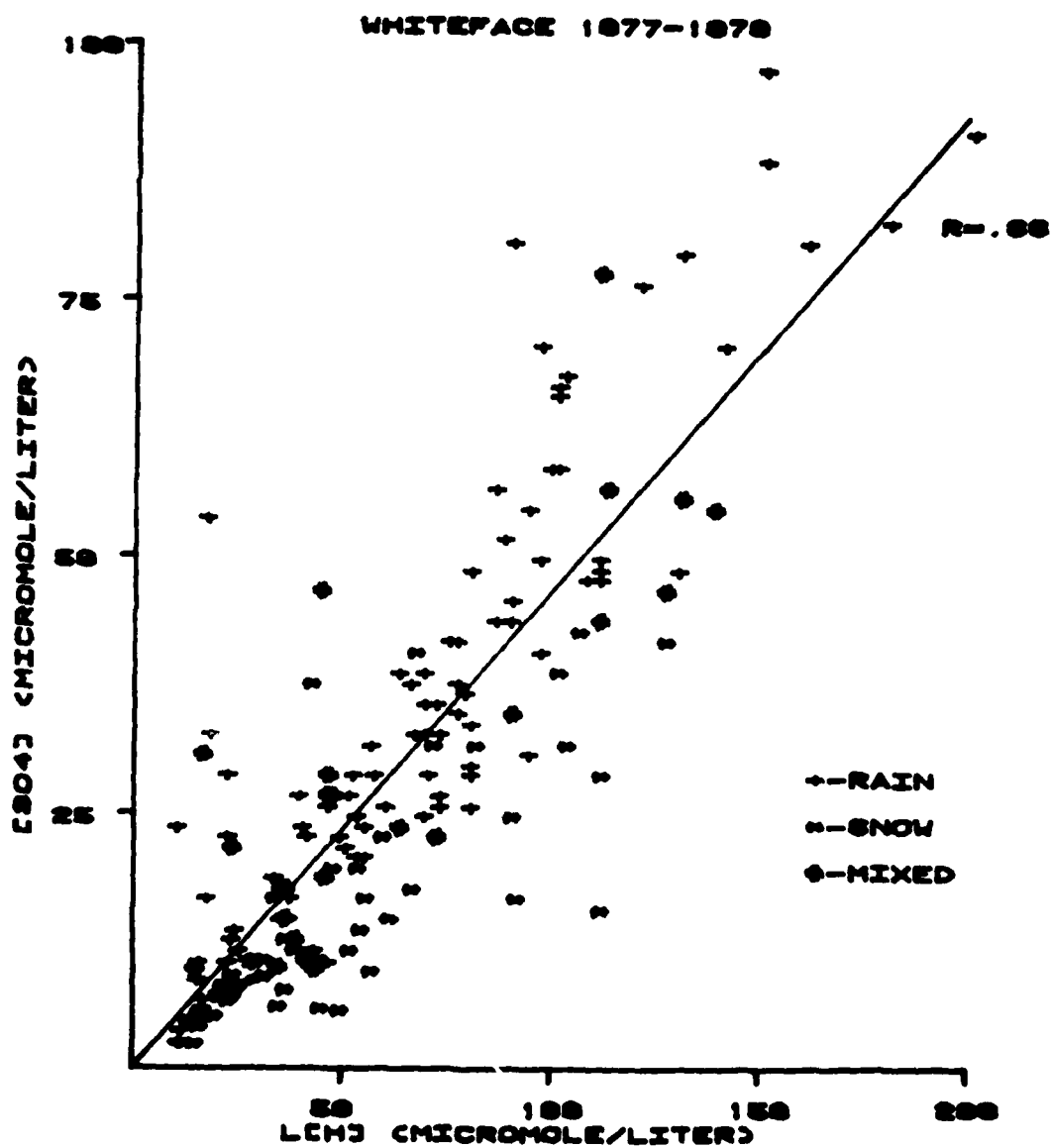


Figure 18. Hydrogen vs. Sulfate for Whiteface, 1977-1979.

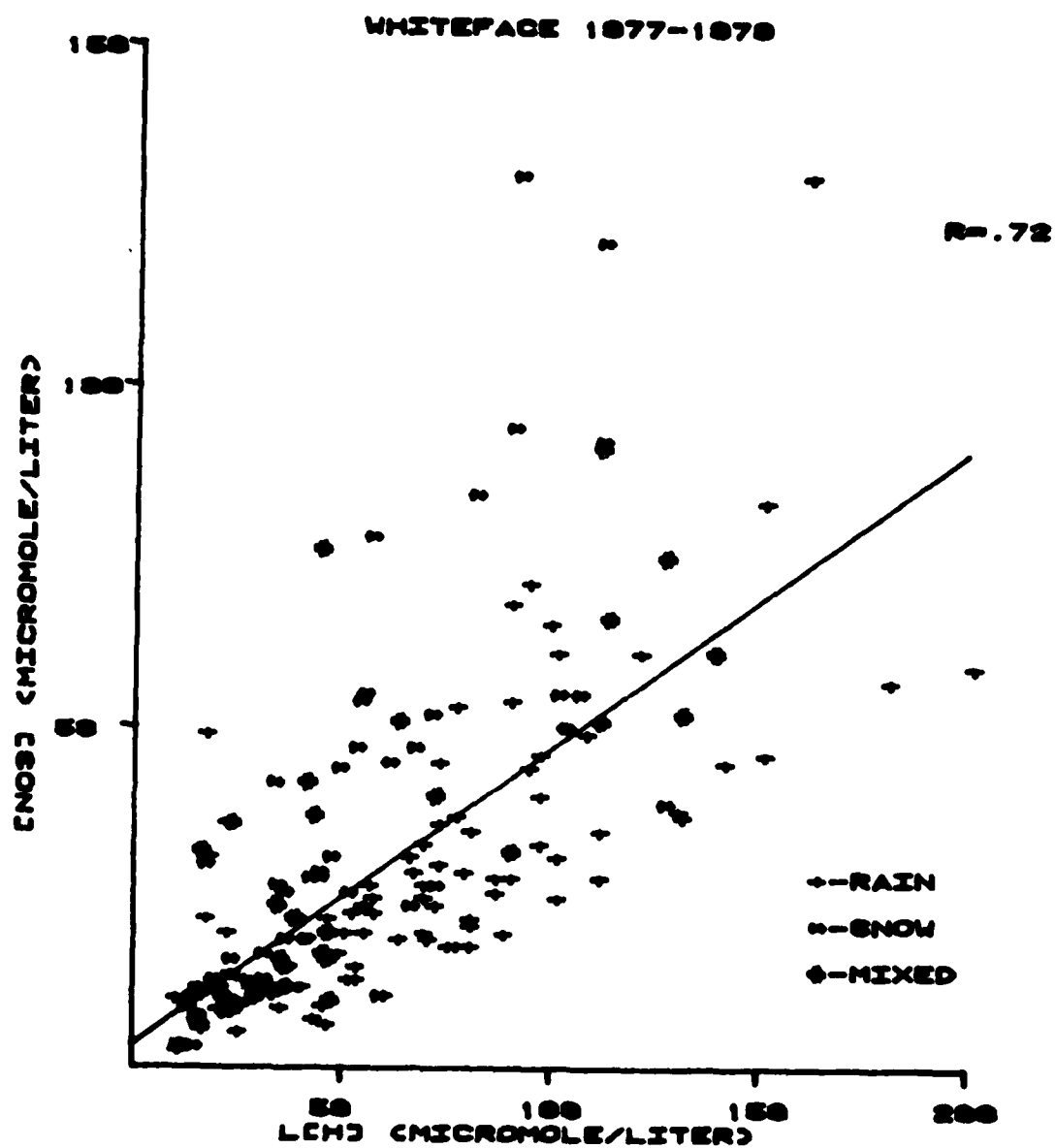


Figure 19. Hydrogen vs. Nitrate for Whiteface, 1977-1979.

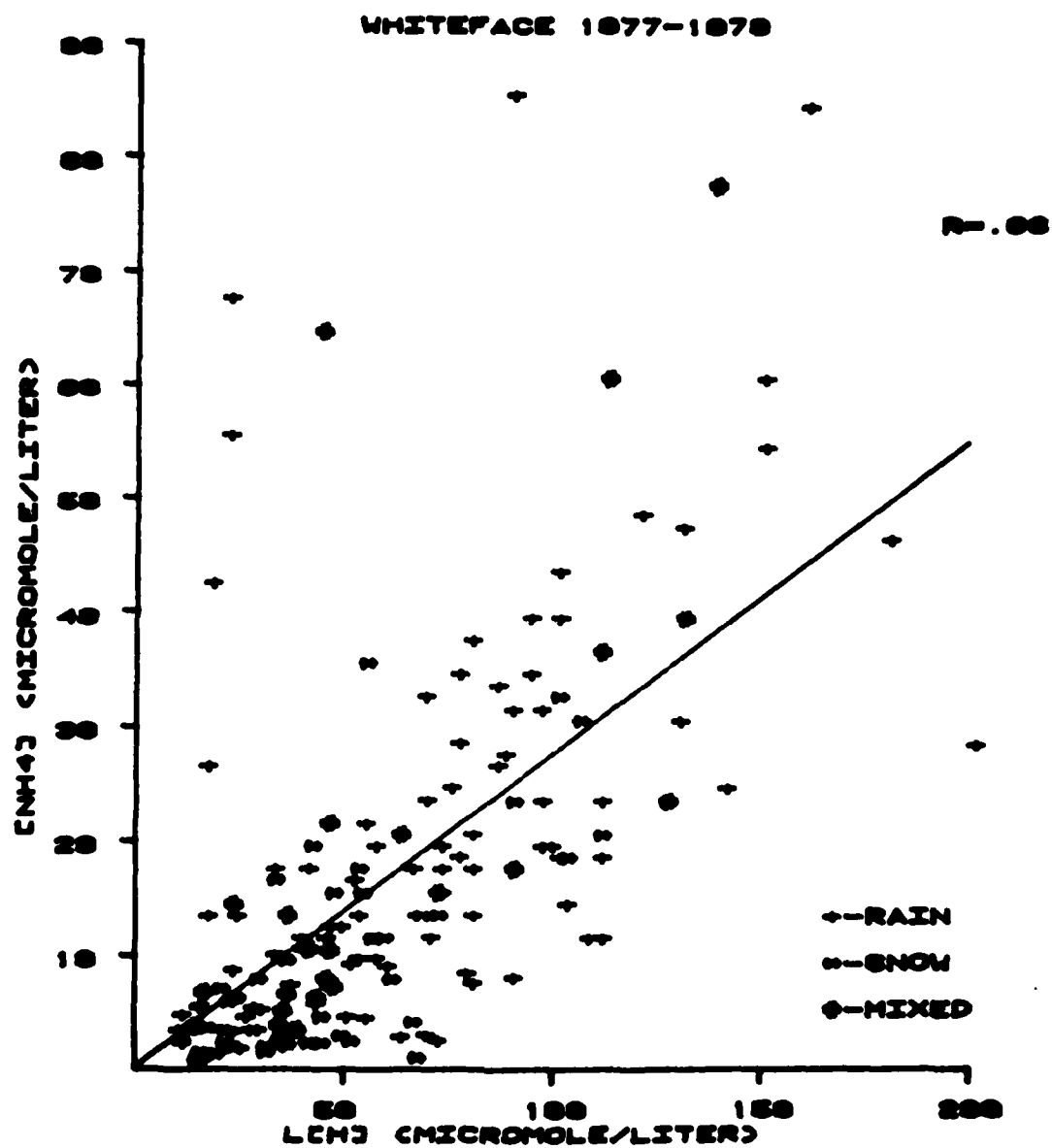


Figure 20. Hydrogen vs. Ammonium for Whiteface, 1977-1979.

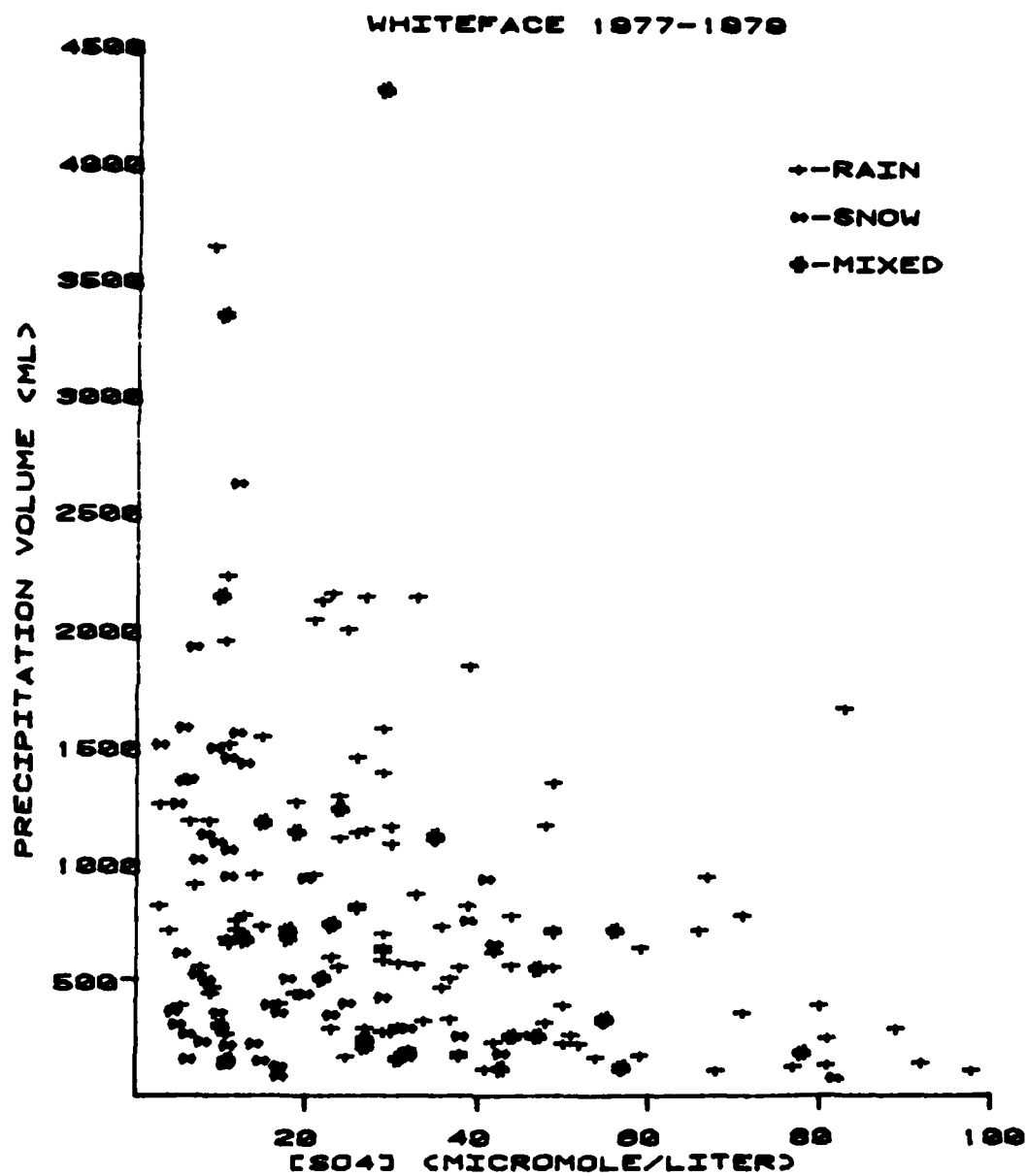


Figure 21. Precipitation Volume vs. Sulfate Concentration for Whiteface, 1977-1979.

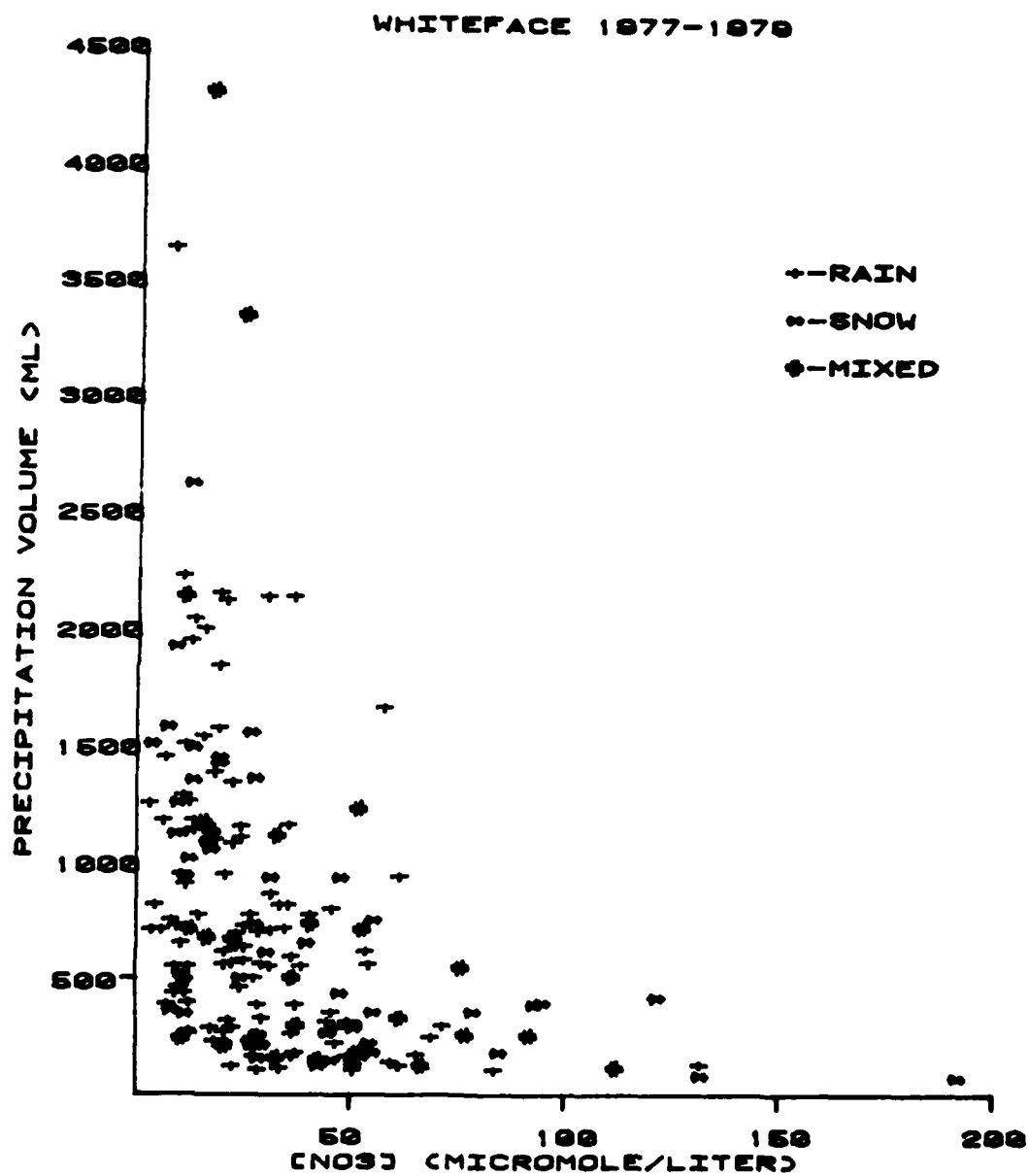


Figure 22. Precipitation Volume vs. Nitrate Concentration for Whiteface, 1977-1979.

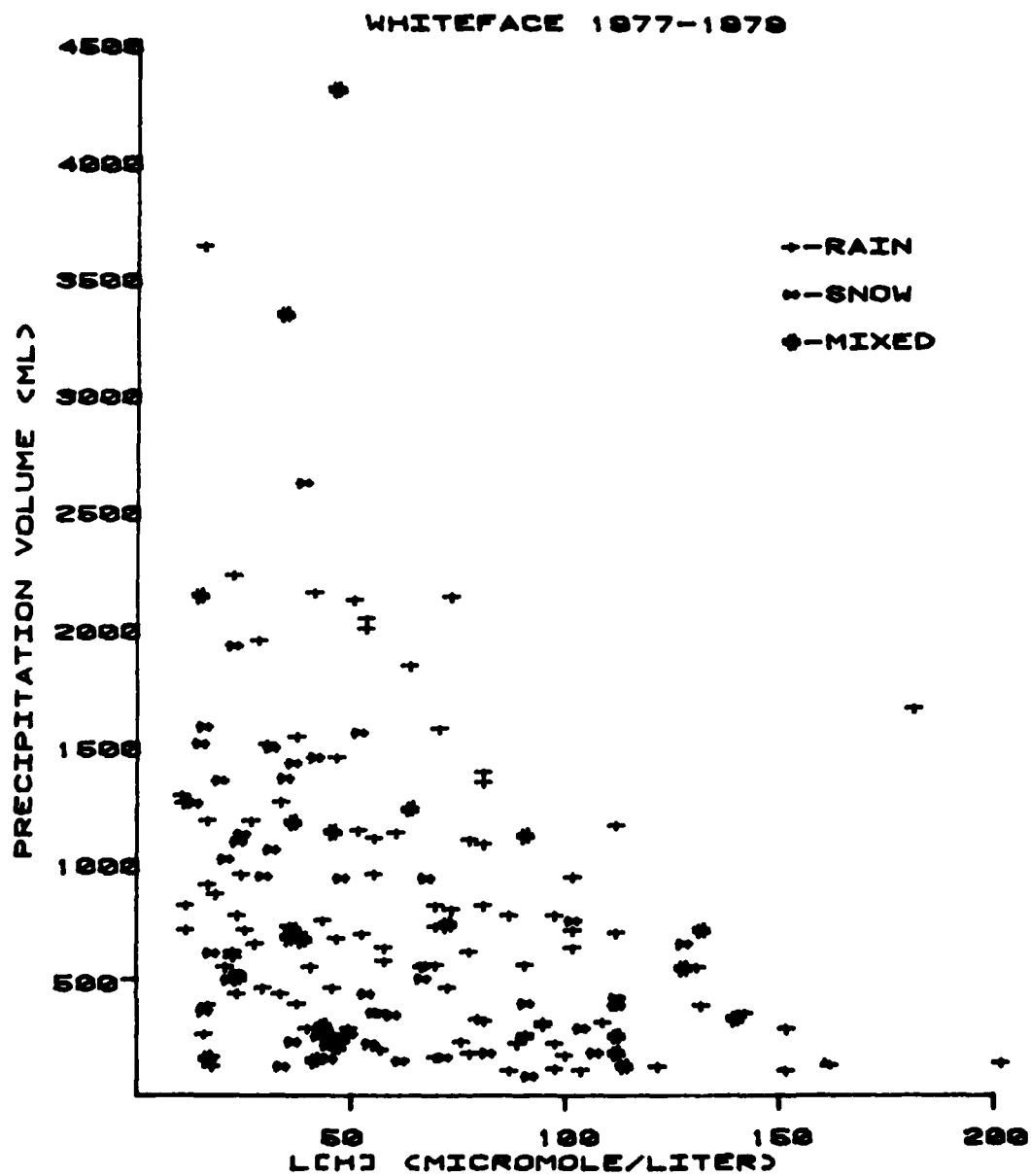


Figure 23. Precipitation Volume vs. Free Hydrogen Ion Concentration for Whiteface, 1977-1979.

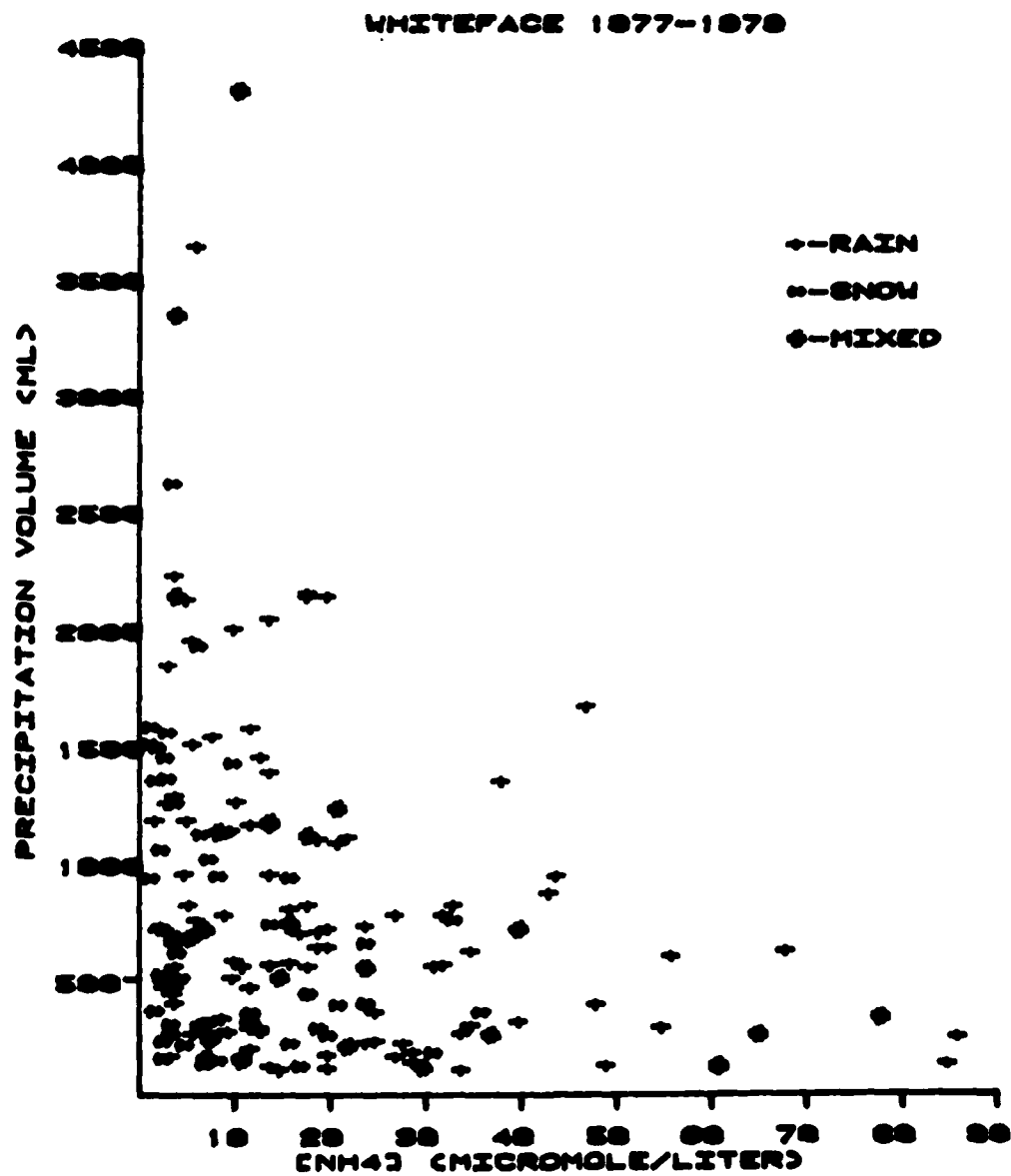


Figure 24. Precipitation Volume vs. Ammonium Concentration for Whiteface, 1977-1979.

2.7 Significant Event Analysis

It is conceivable that massive amounts of pollutants delivered in precipitation over a relatively short period of time could be more detrimental than large cumulative totals over one or more months. This study will not try to resolve this question, but rather examine case studies which have the potential for significant deposition.

As previously defined, a significant event or deposition episode is one whose value exceeds the annual mean by one standard deviation. Frequency plots were generated for concentration and deposition to determine mean values as well as significant events. Regional averages (represented by the sum of all significant events for all four stations over a three-year period) were determined for the percentage of significant deposition events with the following results:

	$[\text{SO}_4^{=}]$	$[\text{NO}_3^{-}]$	$[\text{H}^{+}]$
% of significant events for region	12%	12%	13%

It follows that over the entire region, about 12% of the precipitation events deposit sulfate, nitrate, and hydrogen ions in excess of one standard deviation beyond the mean.

Table 14 summarizes these deposition results with the ratio of the significant event to the annual total, the percentage of the total, and the date of collection for the four basic MAP3S stations. Over the three-year period 1977-1979, there were an average of 62 collection events per year for the four stations. No particular pattern emerges as far as their geographic distributions are concerned, i.e., all stations can experience equally high values at some time over the

TABLE 14

Station	Year	(SO ₂) _{max}				(NO ₂) _{max}				Significant Deposition Events (maximum annual deposition)			
		(SO ₂) _{max} [mg/m ²]	Percent of annual	Date when max. occurred	(NO ₂) _{max} [mg/m ²]	Percent of annual	Date when max. occurred	(H ₂) _{max} [mg/m ²]	Percent of annual	Date when max. occurred	(H ₂) _{max} [mg/m ²]	Percent of annual	Date when max. occurred
WPN	1977	132/2333	5.7	9-14	96/1495	6.4	10-18	3.006/46.5	6.6	9-14			
	1978	262/1908	13.7	8-30	115/1091	10.5	8-30	5.991/41.2	14.5	8-30			
	1979	234/1908	12.3	10-9	80/1346	5.9	10-9	3.919/47.1	8.3	10-9			
ITRACA	1977	216/2233	9.7	7-20	122/1336	9.1	10-17	4.285/41.5	10.3	4-29			
	1978	159/2351	6.8	8-10	80/1401	5.7	7-1	2.767/49.3	5.6	8-10			
	1979	253/2429	10.4	7-24	88/1346	6.5	10-6	5.117/62.0	8.3	7-24			
PDM STATE	1977	174/2698	6.4	9-27	90/1716	5.7	9-27	3.954/53.7	7.4	9-27			
	1978	220/2448	9.0	6-4	97/1583	6.1	6-4	5.219/56.6	9.2	6-4			
	1979	336/3188	10.5	11-4	219/1983	11.0	11-4	4.138/75	5.5	2-27			
VINCINIA	1977	323/1744	18.5	5-31	143/897	15.9	5-31	6.661/31.5	21.1	5-31			
	1978	185/2284	8.1	8-28	114/1273	9.0	7-5	3.821/55.7	6.9	7-5			
	1979	136/1620	8.4	8-19	60/913	6.6	2-13	4.081/44.0	9.3	9-4			
All station average/year		219/2262			109/1366			4.42/50.3					
Percent of annual			9.7			8.0			8.8				

three year period. Most of the time, deposition episodes for sulfur and hydrogen ions occur simultaneously. The overall summary, i.e., the regional average for all stations and for the three year period 1977-79, shows that the maximum event concentration for such a deposition episode is between 8-10% of the annual total deposition (from Table 14):

	$\frac{(\text{SO}_4^{=}) \text{ max.}}{(\text{SO}_4^{=}) \text{ annual}}$	$\frac{(\text{NO}_3^{-}) \text{ max.}}{(\text{NO}_3^{-}) \text{ total}}$	$\frac{(\text{H}^{+}) \text{ max.}}{(\text{H}^{+}) \text{ total}}$
All station average per year (mg/m ²)	219/2262	109/1366	4.42/50.3
Percent of annual	9.6%	8.0%	8.8%

It should be noted that an event may extend over several days in some cases and the date of occurrence is actually the date of MAP3S collection.

It is particularly interesting that the maximum event deposition dates for the various ions are not necessarily the same for each station. That is, mechanisms other than the dominant influence of precipitation volume appears to be at work during some events leading to deposition episodes. Elevated concentration levels would be the logical source for these maximized events. Also many of the events did not occur in the summer months when atmospheric loading with photochemically-induced secondary pollutants is usually highest.

As an extension of these data, Table 15 provides a more detailed look at the variables for these events, including precipitation time. It is immediately obvious that the large values of sample volume is

one of the dominant factors influencing "deposition episodes" since all but two events had sample volumes of over 1000 ml. It also suggests that there must be an optimum combination of the concentration values for various ions as well as amount of precipitation delivered. Large values in precipitation, such as occurred during Hurricanes David and Frederic, with below average or very low ion concentrations, do not constitute a deposition episode. Hurricanes David and Frederic will be extensively discussed in Chapter 3.

It can be concluded that deposition episodes do indeed occur at all stations with large amounts of pollutants delivered in a relatively short time span. No particular pattern emerges as far as their geographic distributions are concerned. Finally, there appears to be no preferred season for the occurrence of these episodes, since they rely on the optimum combination of concentration and precipitation amounts.

TABLE 15

Station	Date of Maximum Event Deposition	Sample Volume (ml)	Ion concentration ($\mu\text{mole/L}$) coinciding with maximum event deposition				Maximum event deposition (mg/m^2) for 1977, 78, 79, respectively ("Deposition Episodes")				Precip. Time (Hrs.)
			$\text{L}[\text{H}^+]$	$[\text{SO}_4^{--}]$	$[\text{NO}_3^-]$		SO_4^{--}	NO_3^-	H^+		
WFM	14 Sep. 77	2100	72	32	35		132	-	3.09		45
	18 Oct. 77	4850	33	9	23		-	96	-		48
	30 Aug. 78	1631	180	82	56		262	115	5.99		22
	9 Oct. 79	4267	45	28	15		234	80	3.92		34
ITH	29 Apr. 77	2100	100	45	32		-	-	4.28		68
	20 Jul. 77	670	350	230	63		216	-	-		12
	17 Oct. 77	2690	71	29	39		-	122	-		37
	1 Mar. 78	110	190	46	190		-	80	-		10
	10 Aug. 78	1130	120	72	25		159	-	2.77		9
	24 Jul. 79	1990	126	65	25		253	-	5.12		5
	6 Oct. 79	2900	78	32	24		-	88	-		15
	27 Sep. 77	2691	72	33	29		174	98	3.95		19.3
PEN	4 Jun. 78	1023	250	110	75		220	97	5.22		5
	27 Feb. 79	2122	96	27	37		-	-	4.14		38.3
	4 Nov. 79	1929	48	89	90		336	219	-		13.5
	31 May 77	1920	170	86	59		323	143	6.66		12
VIR	5 Jul. 78	1076	174	74	84		-	114	3.82		58
	28 Aug. 78	2100	76	45	14		185	-	-		2.3
	15 Feb. 79	1600	45	4	30		-	60	-		10.5
	19 Aug. 79	1145	110	98	67		136	-	-		12.5
	4 Sep. 79	2000	100	34	22		-	-	4.08		7

3.0 TRAJECTORY ANALYSIS OF MAP3S DATA

3.1 The Air Resources Laboratories' Atmospheric Transport and Dispersion Model

While total deposition for the various ions provides valuable information as to the total input, it is equally necessary to have available a sufficiently documented aerometric data base and supporting meteorological information to determine the trajectories of air masses responsible for the precipitation chemistry at a particular site. To this extent, the Air Resources Laboratories' Atmospheric Transport and Dispersion Model (ARL-ATAD), Heffter (1980), was used to develop a trajectory climatology in conjunction with the precipitation chemistry at the Whiteface Mountain and Illinois sites. These locations were chosen since they represent the extreme eastern and western boundaries of the MAP3S network, with the Ohio Valley located in between. The observations from these two stations should provide insight into the contribution of this region to pollutant loading of the atmosphere. Trajectories are also generated for individual events or special case studies such as Hurricane David and Hurricane Frederic (both occurring in September of 1979).

The ARL-ATAD trajectory model offers the flexibility to calculate diagnostic low-level trajectories, either forward or backward in time, for almost any location in North America. Observed upper-level data are used for all computations with average winds in a particular layer computed from values linearly weighted with respect to the depth between mid-reporting levels. If the winds at the station are missing at an observation time, the average wind is linearly interpolated from

computed average winds at the station for six hours before and after observation time. Interpolated winds are assumed to persist three hours before and after observation time.

The transport layer depth (TLD) initially depends upon whether the trajectory begins at day or night. For trajectories beginning at day the daytime scheme is used throughout. The TLD for each station is determined by converting significant and mandatory level temperatures to potential temperatures and then scanning upward from 300 m to determine the lowest critical inversion. A critical inversion is defined as having the following characteristics:

$$\frac{\Delta\theta}{\Delta Z} \geq 0.005^{\circ}\text{K/m}$$

$$\theta_{\text{top}} - \theta_{\text{base}} \geq 2^{\circ}\text{K}$$

where θ_{top} and θ_{base} are the potential temperature of the top and base of inversion layer, respectively. The transport layer depth (TLD) is then defined to be

$$\text{TLD} = \text{TLH} - \text{ATH}$$

where TLD = transport layer height

ATH = average terrain height.

The transport layer height is the height in the critical inversion layer where the temperature is 2°K above the temperature at the inversion base, as shown in Figure 25. When no critical inversion is present, the TLD is assumed to be 3000 m.

The nighttime calculations assume that the transport layer depth (TLD) is approximately equal to:

$$\text{TLD} = 2(2K_z \cdot T)^{1/2}$$

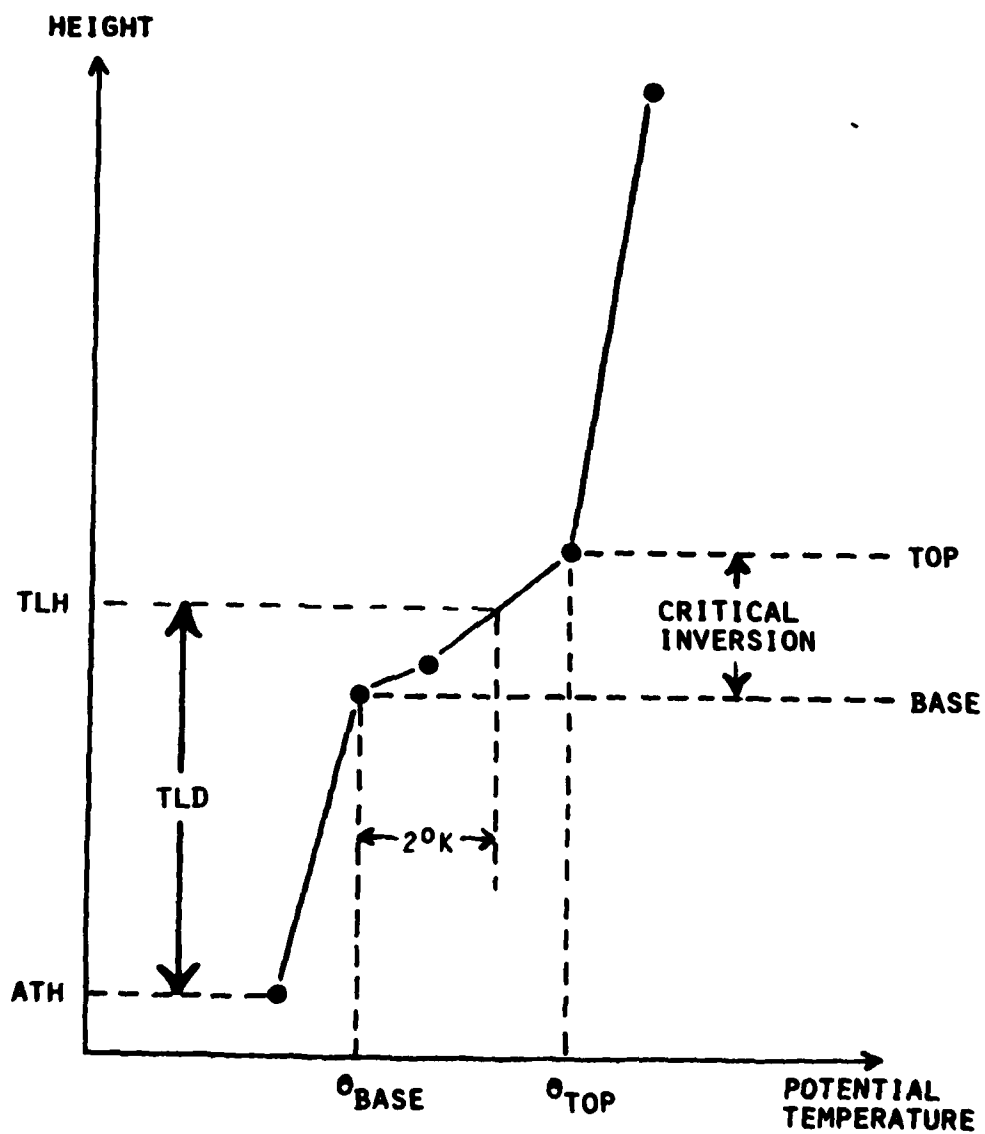


Figure 25. ARL-ATAD model criteria for determining transport layer depth. (Reffter, 1980)

where K_z is the vertical coefficient of eddy diffusion and has the numerical value of $1 \text{ m}^2 \cdot \text{s}^{-1}$ and T is the transport time in seconds. Nighttime conditions are assumed to persist from 00Z to 12Z.

A distance weighting factor is then used to weight the station within a 300 nautical mile radius and advect the air parcels in three-hour time steps.

3.2 Error Estimates of the ARL-ATAD Model

Under certain conditions the errors associated with computer simulation of transport by the atmosphere may be large. Research is currently being conducted to determine the accuracy of the ARL-ATAD model under various meteorological situations using Krypton-85 released from the Savannah River Plant in South Carolina (Heffter et al., 1977). Previous attempts to correlate observed versus calculated ARL-ATAD trajectory endpoints have been made using chlorofluorocarbon data (Pack et al., 1977) and tetroon flights (Pack et al., 1980). These studies found the ARL-ATAD model to provide reasonable estimates of transport and dispersion out to 1000 km.

In order to understand what variations in trajectory endpoint calculations might be expected, the diagnostic ARL-ATAD model was compared to the prognostic National Meteorological Center (NMC) one-day trajectories. While these comparisons will not provide an absolute verification of either model, it will generate trajectory analysis from separate, distinct sources which can serve as a basis for a discussion of model weaknesses.

The NMC trajectory model offers improved low-level forecasts of temperature and moisture since all available upper-air data for land and ship stations are used in the initialization of the trajectory origin. The Limited Fine Mesh model (LFM) uses only mandatory level data (Gerrity (1977)). Additionally, a reduced smoothing function allows for steep gradients in temperature and moisture along the air parcel path.

The trajectory model uses the wind forecasts at six-hour intervals of the LFM-II model for 1000 mb, 850 mb, 700 mb, 500 mb, and 300 mb. Then, as with the ARL-ATAD model, trajectories are computed backward in time from selected locations. An initial position is estimated by the advective equation:

$$X_2(t-\sigma t) = X_1(t) - U_1(t)\sigma t$$

where $X_2(t-\sigma t)$ = computed upwind position on X-axis

$$U_1(t) = \text{wind component at point } X_1(t)$$

σt = time iteration (usually 2 hours).

Further refinements in the trajectory location are then obtained by using

$$X_3(t-\sigma t) = X_1(t) - \frac{1}{2}[U_2(t-\sigma t) + U_1(t)]\sigma t$$

where $U_2(t-\sigma t)$ = interpolated value of U at point $X_2(t-\sigma t)$.

Successive iterations of the above equation are performed until the trajectory positions fall within specified convergence criteria, usually taken as 0.01 grid interval and 1.0 mb. This scheme is also utilized in the vertical and between different prognostic fields in order to maintain continuity. Since vertical velocities are not available by the LFM-II model at the initial time, values are

estimated by a backward advection of the six-hour forecast fields. Terrain influences are included in the model to the extent that trajectories are not allowed to intersect the ground and are displaced at each endpoint if necessary.

In order to compare the performance of the two models, back trajectories for Albany, New York, were computed for July 1979 using the ARL-ATAD model. These trajectory endpoints of approximately sixty time periods 00Z and 12Z were then compared to the NMC teletype data.

Distances were computed between the ARL-ATAD model and the 850 mb and surface trajectories of the NMC model in intervals of six hours. A comparison was not made for the NMC 700 mb trajectories since the ARL-ATAD model did not extend above 3000 m. For comparison purposes the distance between the 850 mb and surface trajectory endpoints of the NMC were also calculated. Figures 26 through 28 show the result of these calculations. The dashed line in each figure connects the mean distance for each time interval.

Figure 26 shows the magnitude of the distances between trajectory endpoints that may be expected when considering two different levels by comparing the NMC 850 mb analysis with that of the NMC surface analysis. While most differences are on the order of 50 km for trajectories of six hours duration, a wide range is evident after 24 hours. This suggests that even moderate amounts of directional shear in the vertical can produce sizable differences in positions after extended time periods. If differences were plotted for time periods greater than 24 hours, the mean curve would probably assume an exponential shape as suggested by Pack et al. (1978).

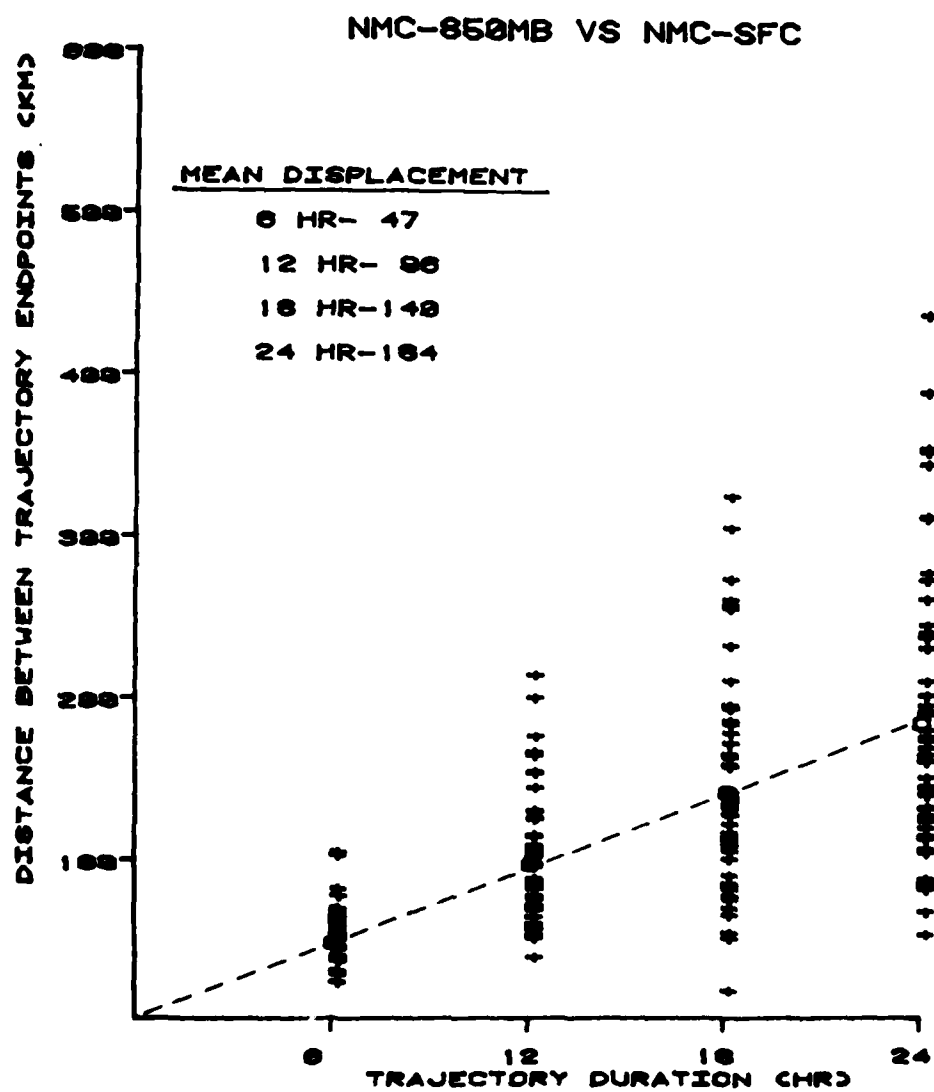


Figure 26. Trajectory endpoint distance between NMC-850mb and NMC-SFC analyses.

Figures 27 and 28 show the trajectory endpoint difference for the ARL-ATAD model versus that of the NMC 850 mb and surface analysis, respectively. The same basic pattern emerges with the mean points connected in a linear fashion. Even though the range of distances is greater in these comparisons, the magnitude of the mean differences or displacements is of the same order. In fact, the mean value of the ARL-ATAD vs. NMC 850 mb differences are less than those of the comparison of the two levels of the NMC model. Figure 27 also shows that only ten percent of the cases after 24 hours were in excess of 300 km for the ARL-ATAD vs. NMC-850 mb comparison.

The diagnostic ARL-ATAD model is therefore found to compare favorably with the prognostic NMC-850 mb analysis for trajectories of duration up to 24 hours. Deviations in trajectory endpoints between these two computations are found to be generally less than the surface and 850 mb endpoint differences for the NMC model. Invalid assumptions of homogeneous layers by the ARL-ATAD model or poor wind field forecasts by the LFM model are two major contributors for discrepancies in trajectory endpoint location.

3.3 Ion Concentration and Deposition vs. Trajectory Sector

3.3.1 Whiteface Mountain (1978)

Since most of the current interest in acid rain is focused on the Northeast, or more specifically, on the Adirondack region of New York State, Whiteface Mountain was again chosen as the prime study candidate. Trajectories were calculated for all of 1978 and 1979 and weighted by precipitation amounts during the concurrent six-hour period to determine a dominant direction or origin of air mass for each MAP3S

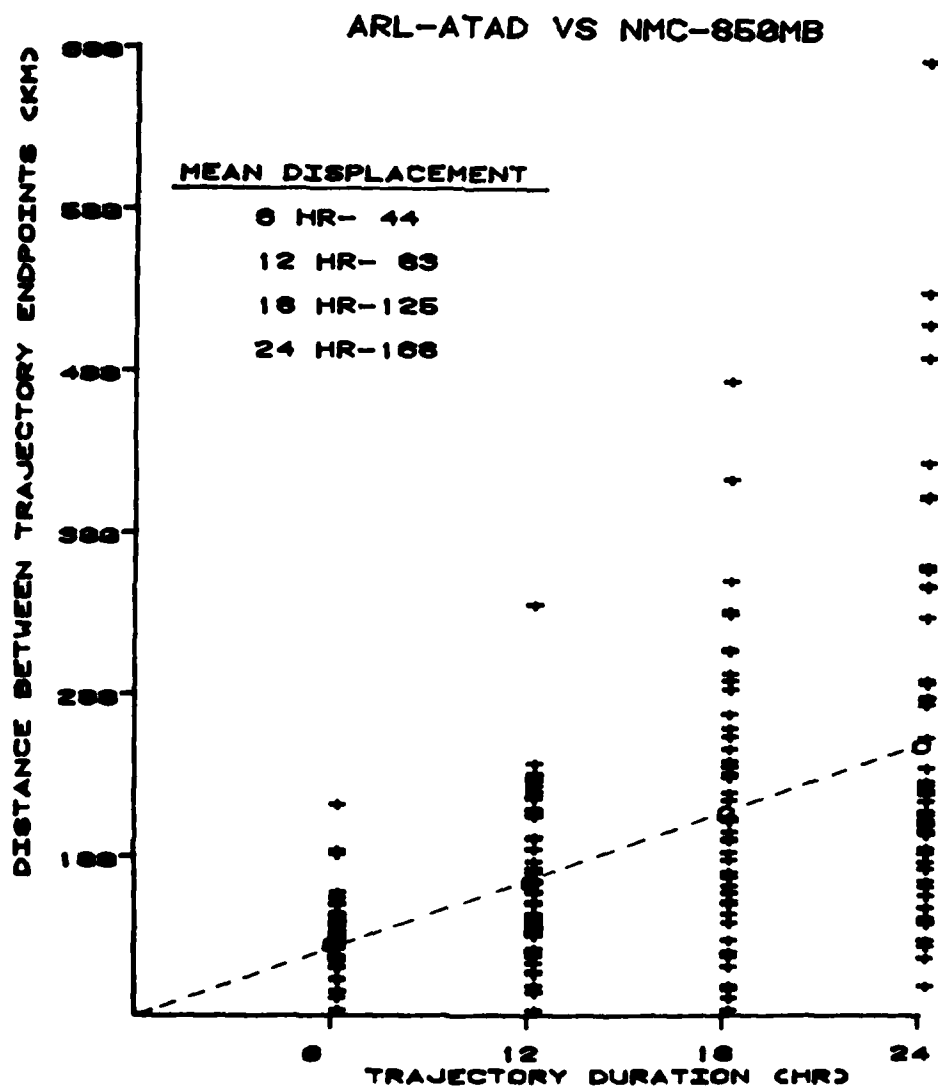


Figure 27. Trajectory endpoint distance between ARL-ATAD and NMC-850mb analyses.

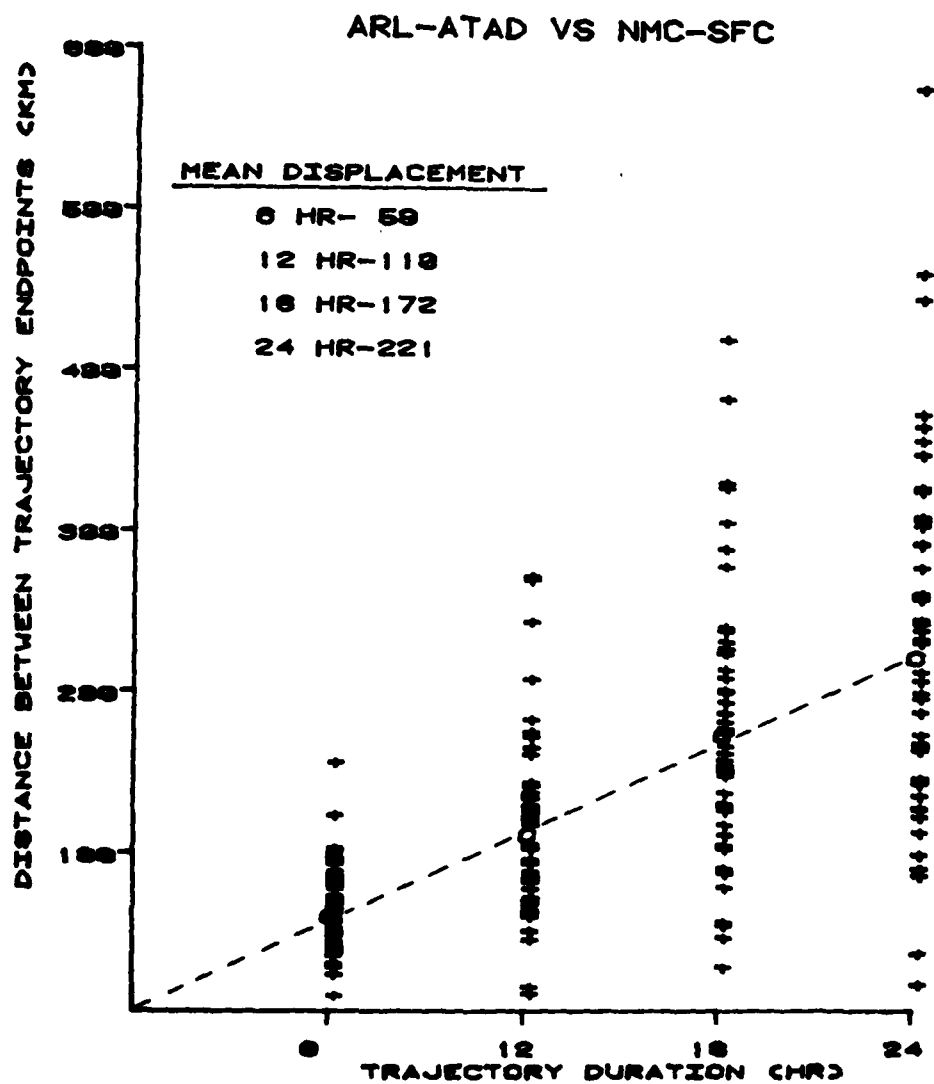


Figure 28. Trajectory endpoint distances between ARL-ATAD and NMC-SFC analyses.

event. Each event was then classified in one of 12-30° sectors. To reduce the sometimes large lateral uncertainty associated with trajectory calculations extending over several days duration, only the final two days (48 hours) of approach trajectory endpoints were considered. This assumption could not provide a complete air mass history. However, the procedure was well suited to classify trajectories into various sectors of origin. This allowed differentiation between so-called "Ohio Valley" and "Canadian" air masses. Even using these assumptions, not all events could be classified as to sector of origin, since some trajectories traversed several sectors during the 48 hours of travel. Furthermore, some MAP3S collection events were actually composed of several smaller separate discrete events with quite different air mass history. However, for 1978, 88% of the precipitation events and of the resulting total wet deposition could be classified by this method. The percentage for 1979 was slightly less at approximately 85% of the precipitation events and 82% of the resulting total wet deposition assigned to a particular compass sector. The results of 1979 appear to be somewhat atypical due to the influence of Hurricanes David and Frederic (September 1979) and therefore will not be extensively discussed.

Figures 29 through 32 show the event concentration and the mean concentration ($\mu\text{mole/liter}$) for H^+ , NH_4^+ , $\text{SO}_4^{=}$, NO_3^- , Na^+ , Ca^{++} , and Mg^{++} as a function of air mass trajectory sector and precipitation type for Whiteface Mountain in 1978. The sectors of the northeast

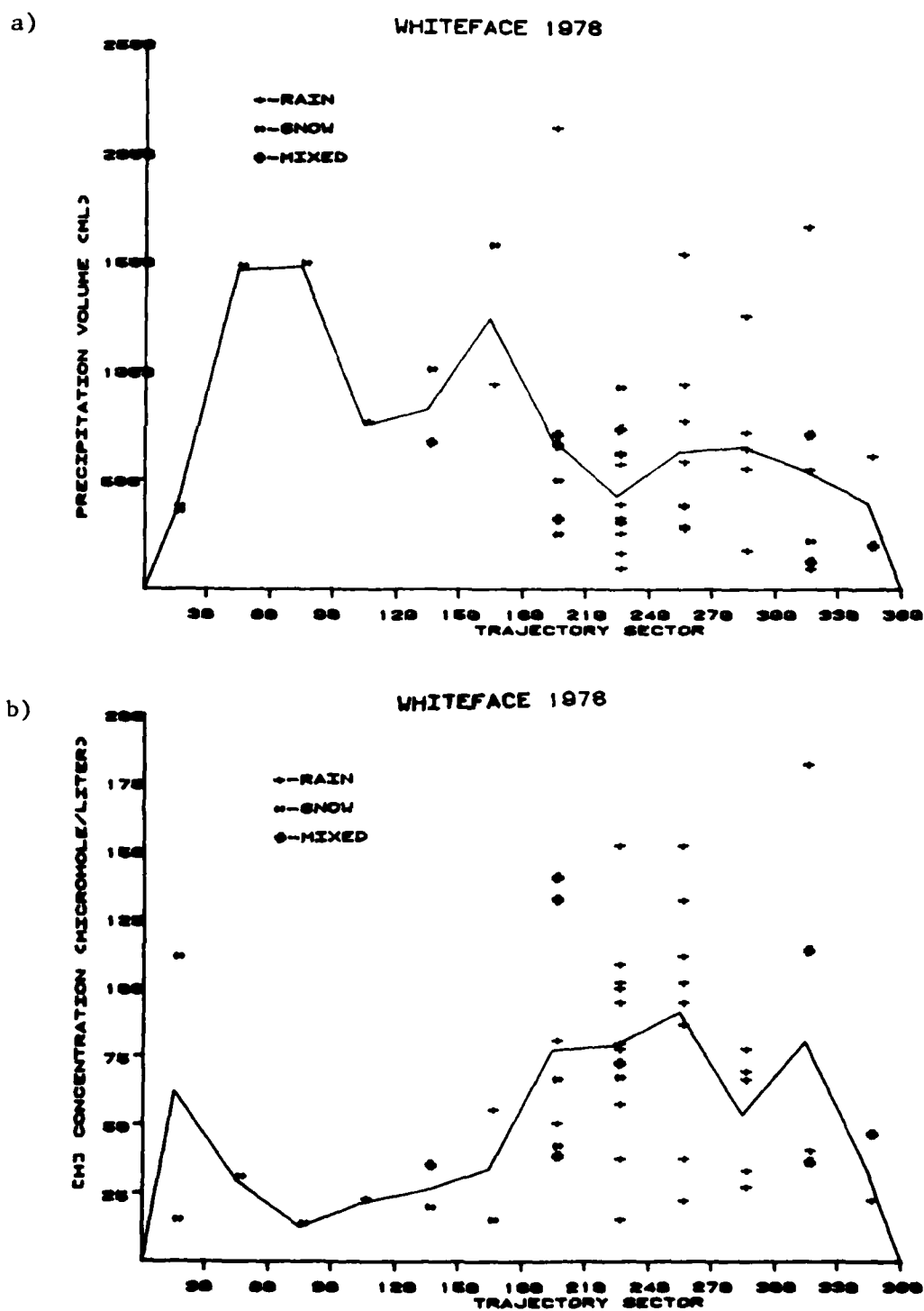
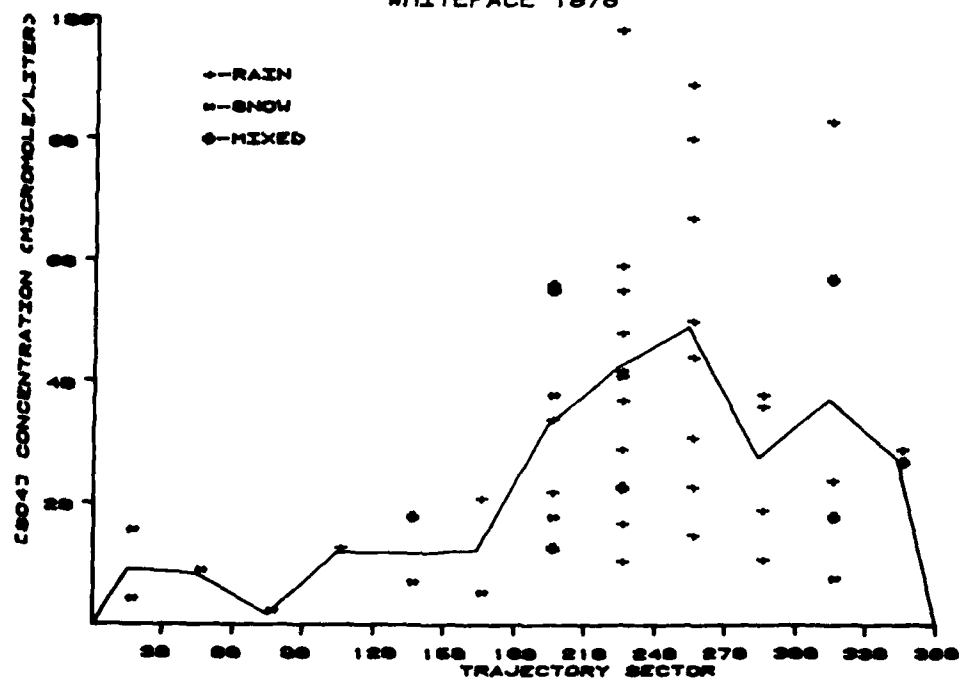


Figure 29. a) Precipitation volume, and b) Free hydrogen ion concentration per 30° trajectory sector for Whiteface, 1978.

a)

WHITEFACE 1978

78



b)

WHITEFACE 1978

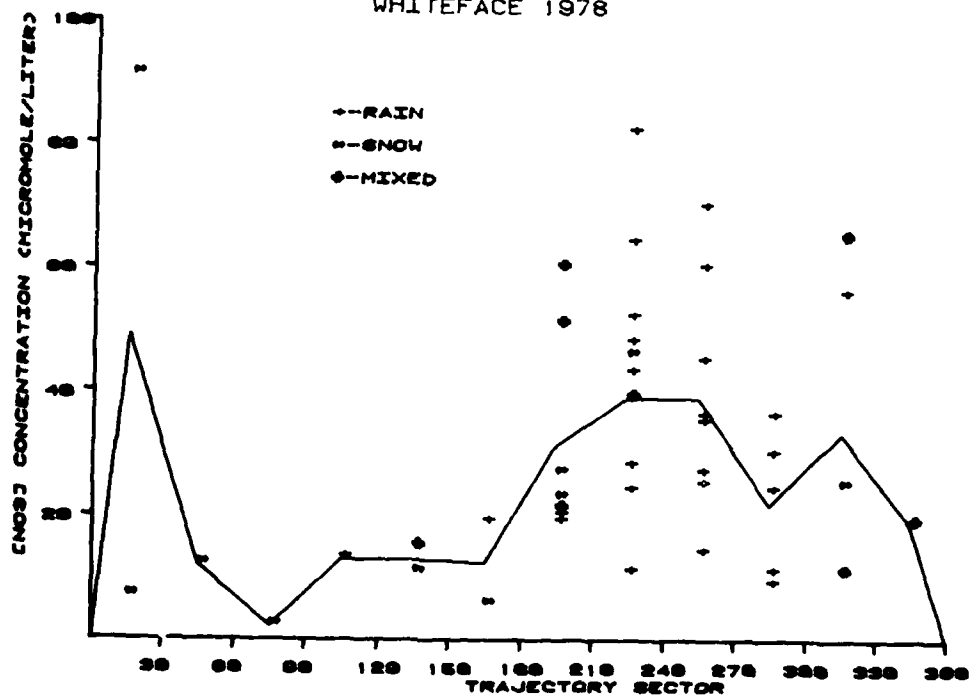


Figure 30. a) Sulfate, and b) Nitrate concentration per 30° trajectory sectors for Whiteface, 1978.

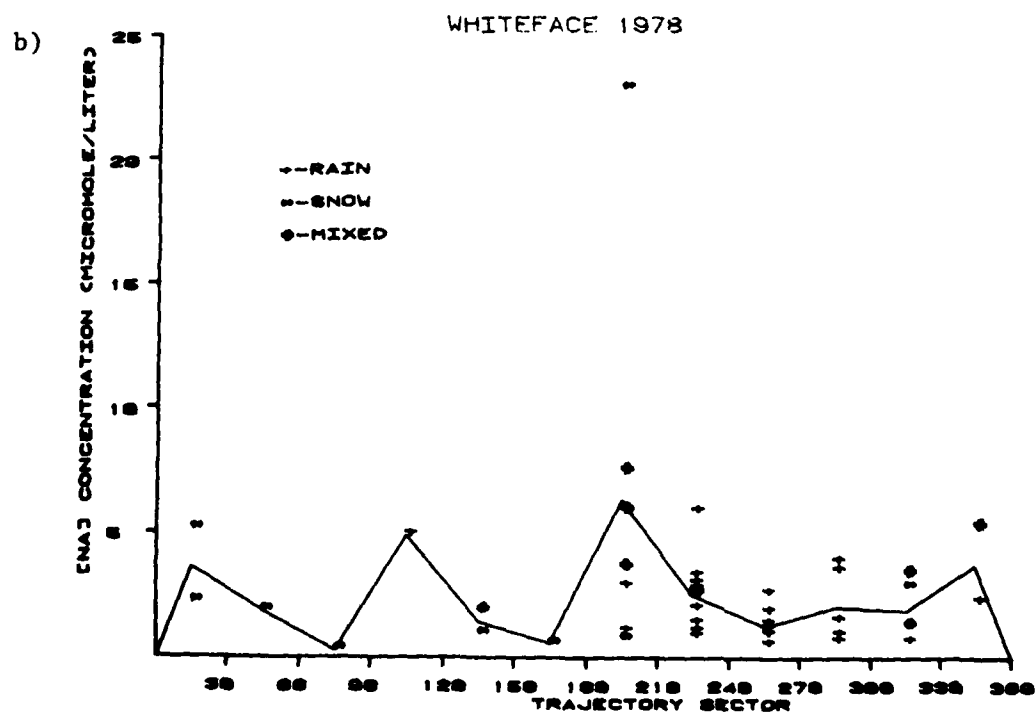
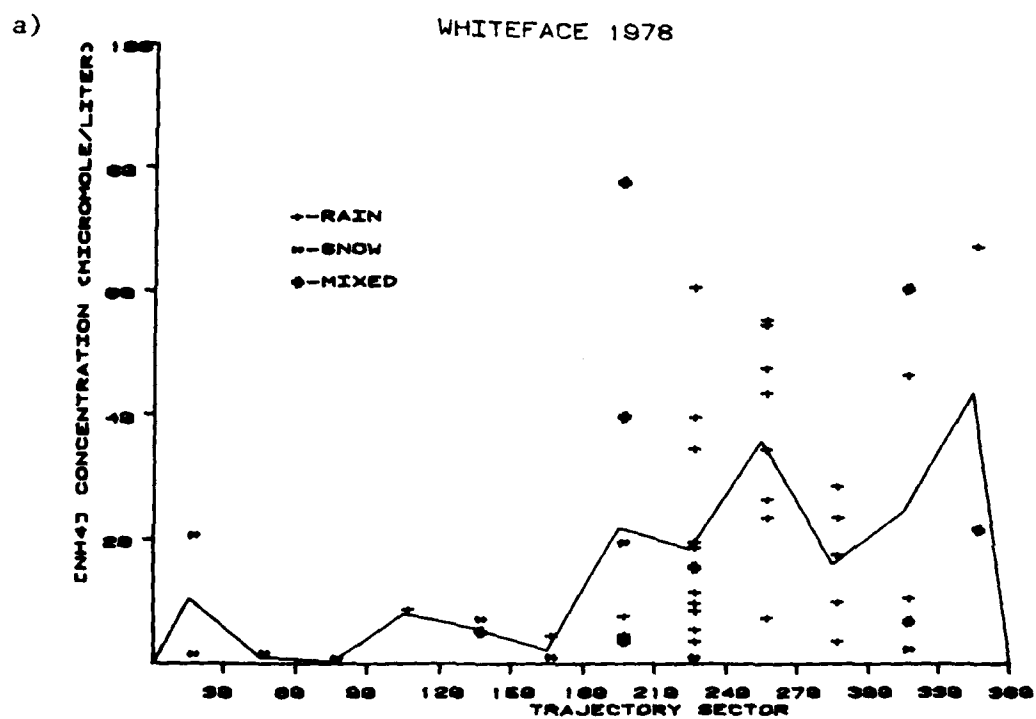


Figure 31. a) Ammonium, and b) Sodium concentration per 30° trajectory sector for Whiteface, 1978.

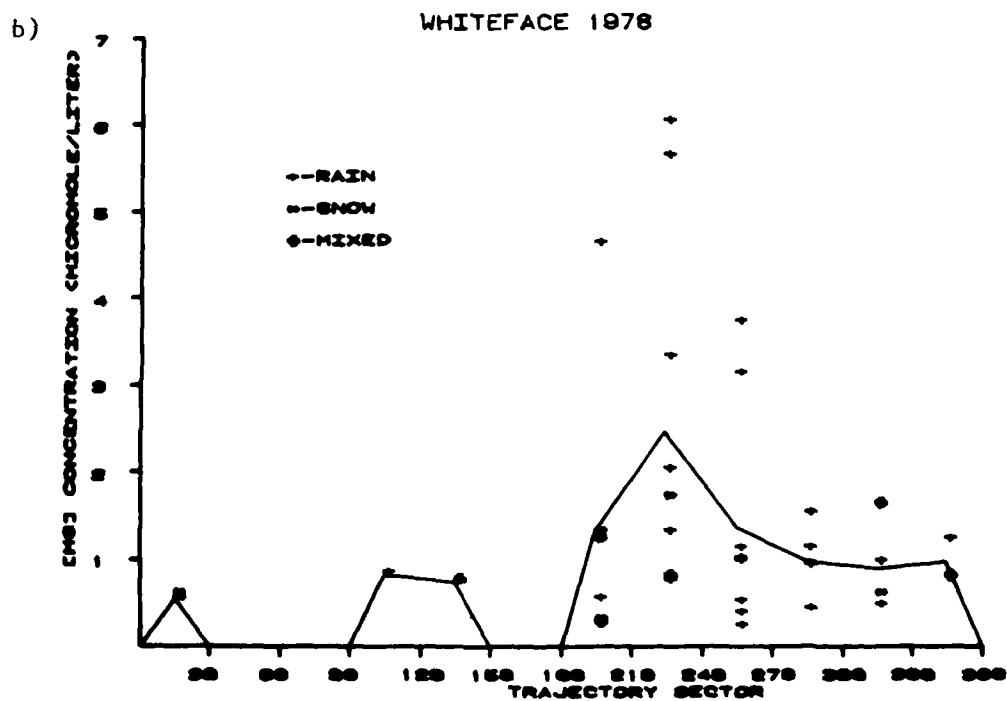
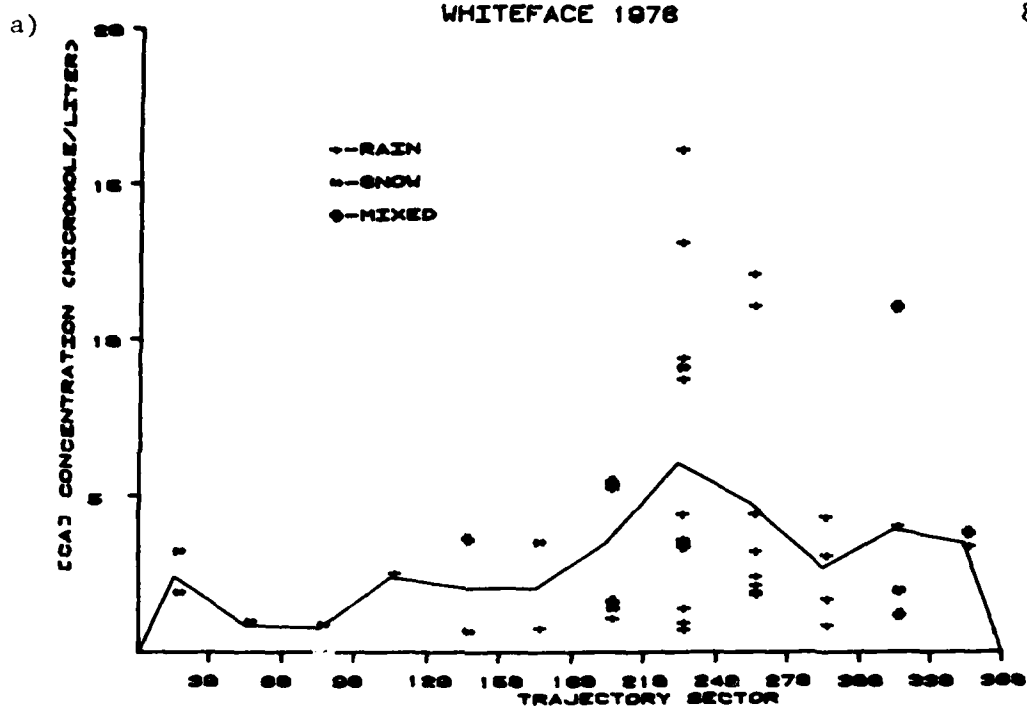


Figure 32. a) Calcium, and b) Magnesium concentration per 30° trajectory sector for Whiteface, 1978.

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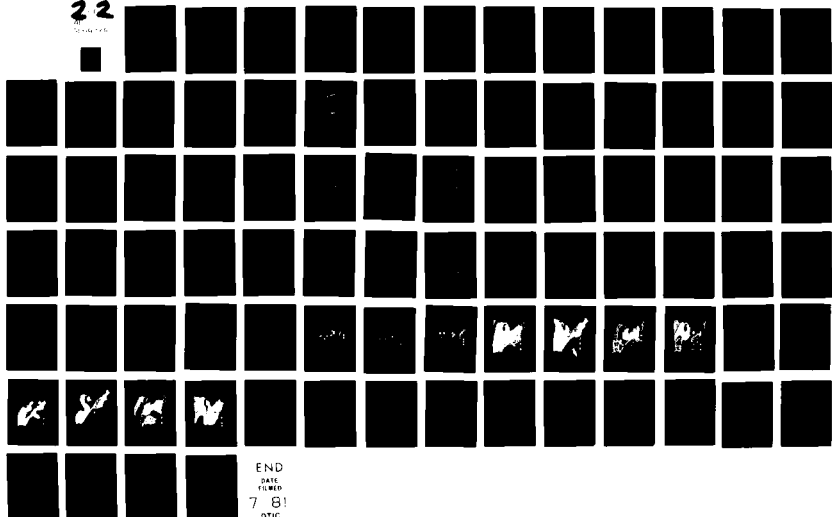
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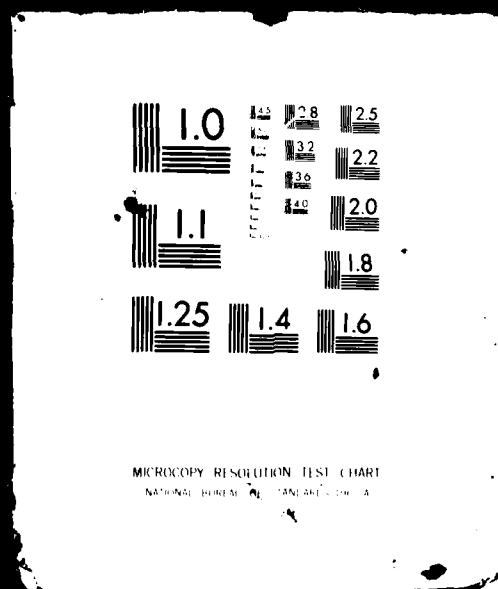


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quadrant contain relatively few data points (few precipitation events) and may not be statistically significant, but do provide insight into the chemical composition and past 48-hour air mass history of several events.

Figure 29a illustrates the precipitation associated with each event and the mean for each sector. The impact of the large coastal snowstorms of a northeasterly component is readily apparent in the 0° - 90° sector. The remainder of the sectors exhibit a relatively large range in precipitation amounts, as might be expected. Figures 29 through 32 demonstrate the variability in event concentration of various ions, while hinting to a general maximum in the mean concentration of the four major ions for the southwest sector. The wide range in concentration for each sector is partially explained by the variability in precipitation amounts for each event. High concentrations are sometimes associated with relatively low precipitation sample volumes indicating a diluting effect with increased amounts of precipitation. While the four dominant ions, H^{+} , $SO_4^{=}$, NO_3^{-} , and NH_4^{+} , seem to exhibit generally higher concentrations for the southwest sector, the ions of Na^{+} , Ca^{++} , and Mg^{++} appear to be independent of approach sector. This might be expected since these neutralizing components are found within the boundary layer and are not usually associated with regional or long-range transport.

A more meaningful analysis emerges if wet deposition (mg/m^2) is plotted as a function of trajectory sector. This approach provides a weighting function and reduces the scatter associated with small precipitation volumes. Figures 33 through 35 show the total wet

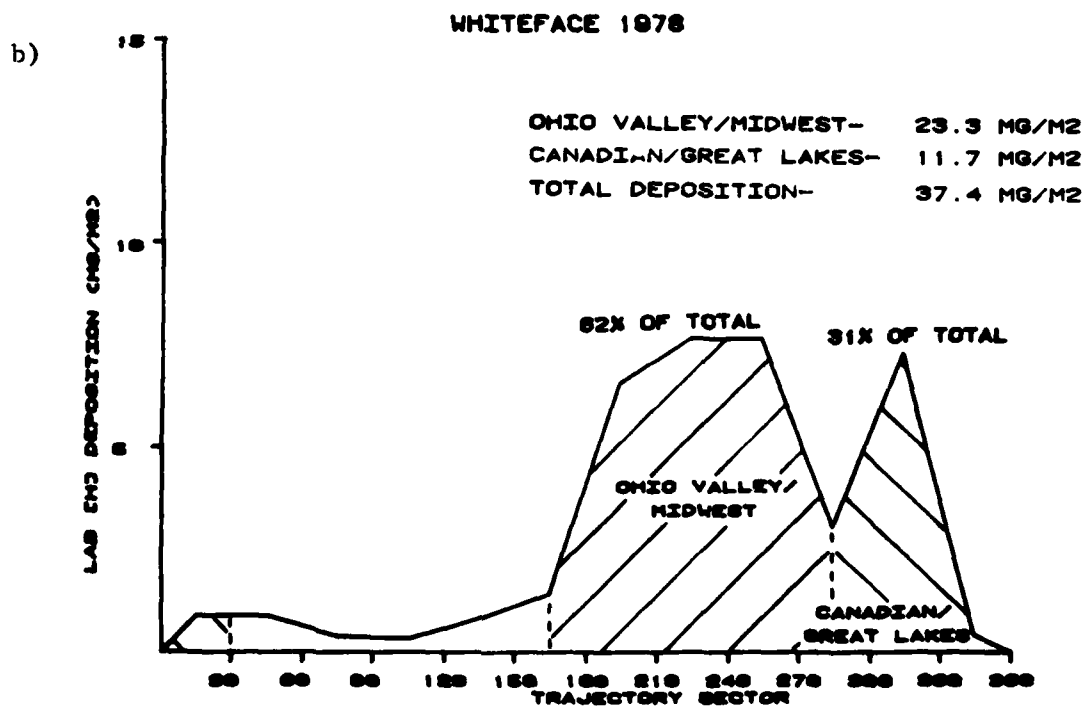
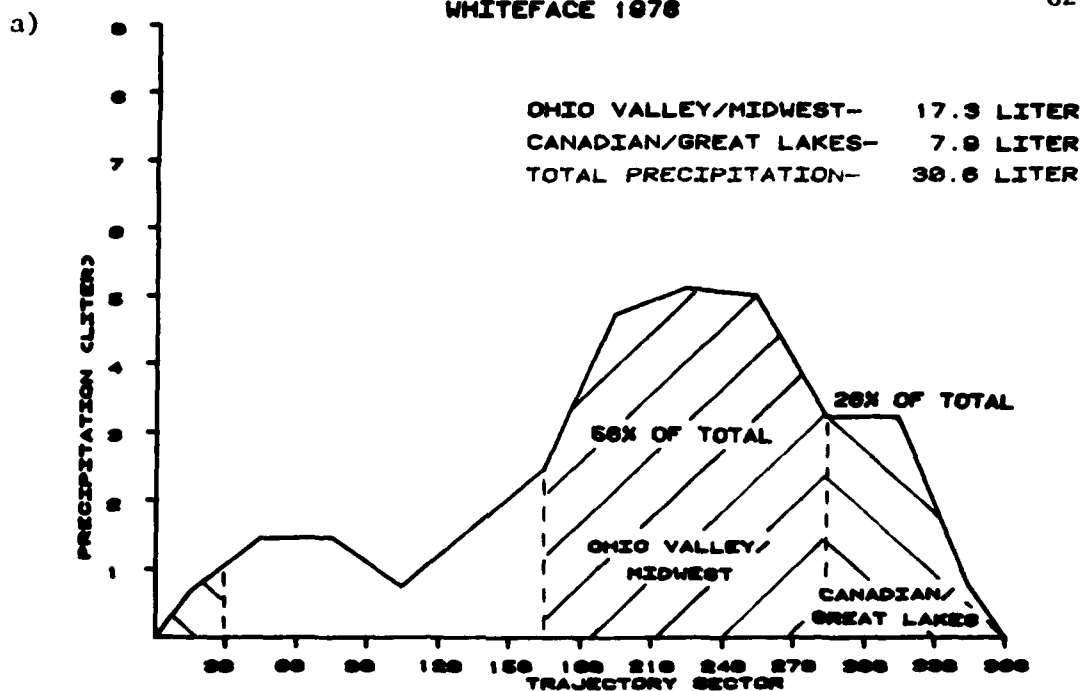


Figure 33. a) Precipitation volume, and b) Free hydrogen ion total wet deposition per 30° trajectory for Whiteface, 1978.

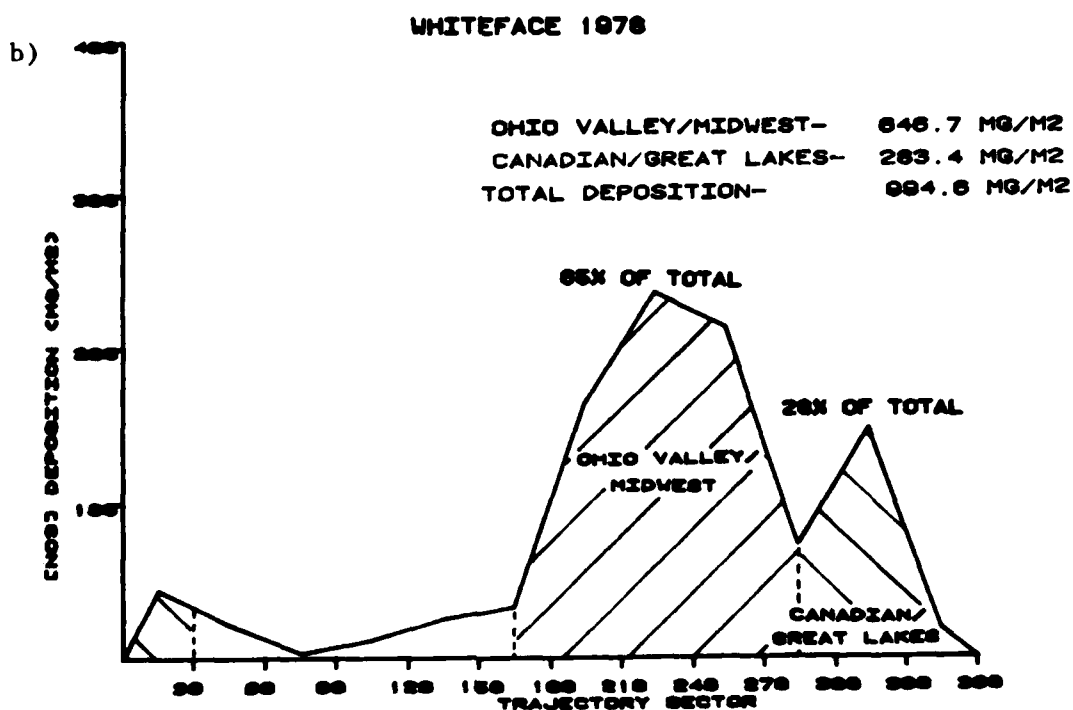
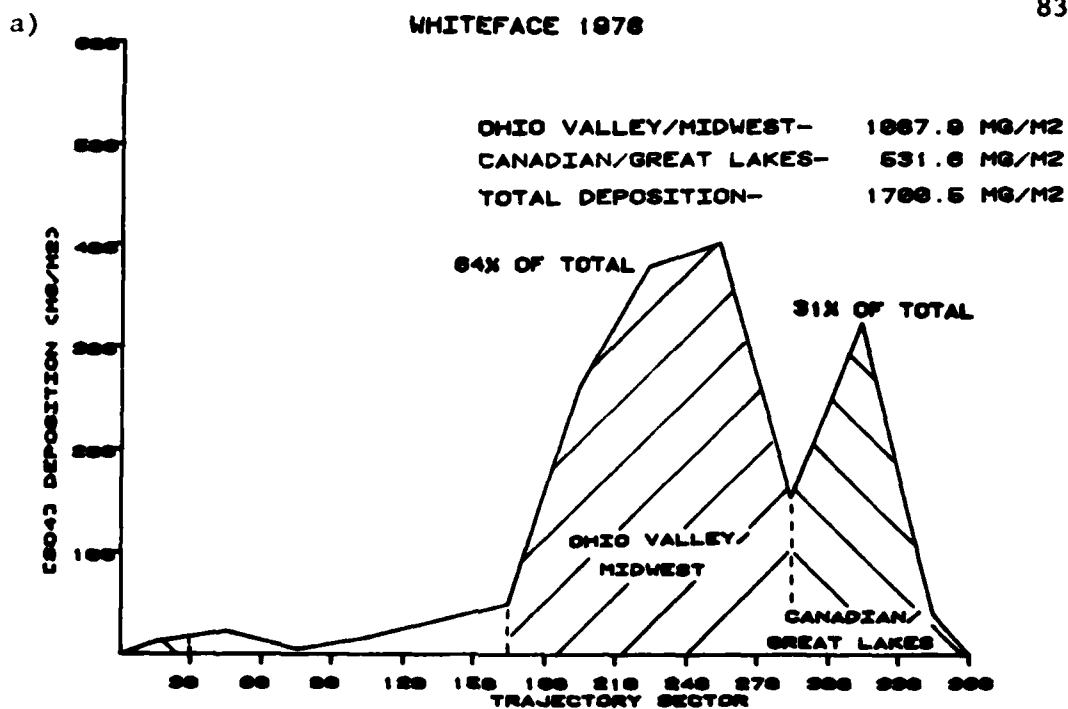
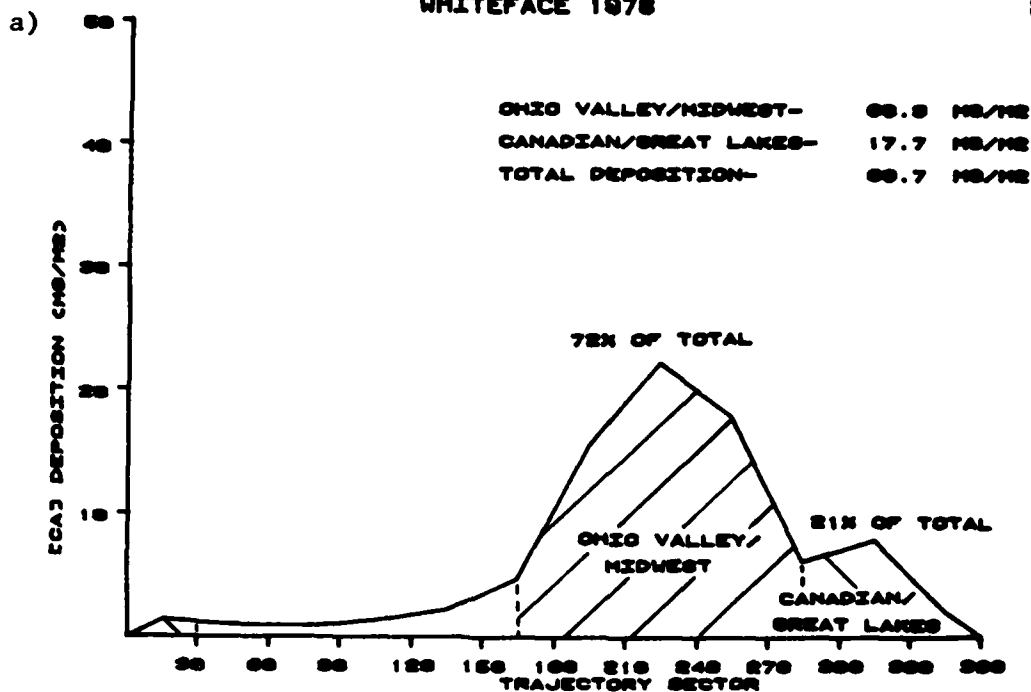


Figure 34. a) Sulfate, and b) Nitrate total wet deposition per 30° trajectory sector for Whiteface, 1978.

WHITEFACE 1978

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WHITEFACE 1978

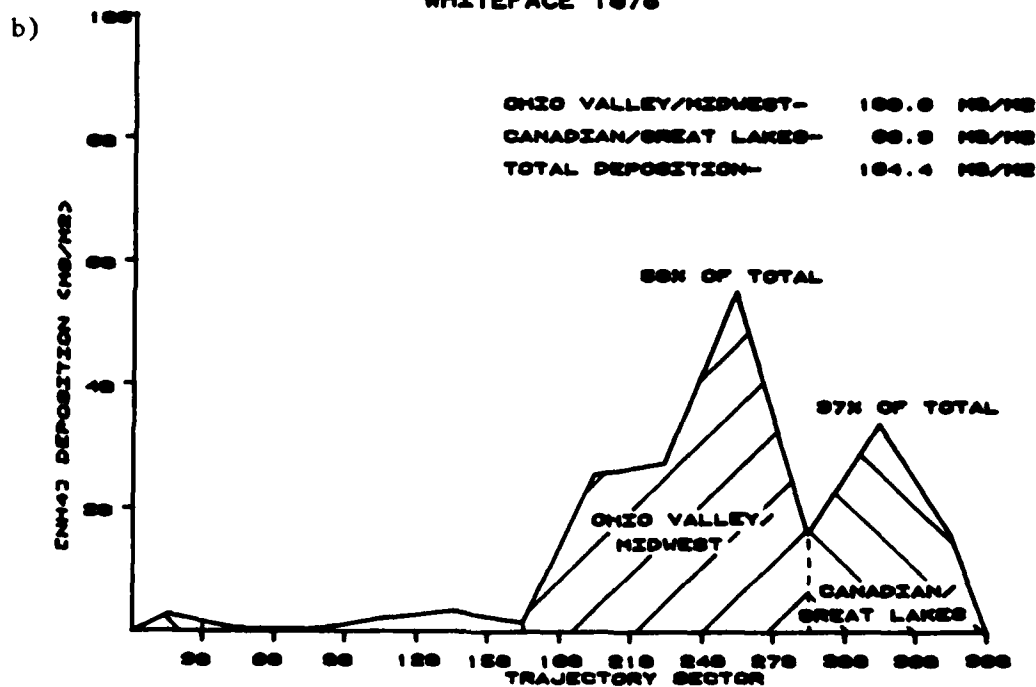


Figure 35. a) Calcium, and b) Ammonium total wet deposition per 30° trajectory sector for Whiteface, 1978.

deposition for the events for Whiteface Mountain that could be classified as a function of trajectory sector or air mass origin. It should be noted that the "total wet deposition" noted on these figures refers to the "total" of the events definable by air trajectory analysis (the ATAD model providing 48 hour back trajectories) and not to the "total" precipitation volume.

The majority of the wet deposition could be further subdivided into two distinct groups: "Ohio Valley/Midwest" events were defined as those having their origin in the sector 165° - 285° , while "Canadian/Great Lakes" was designated by the sector 285° - 30° .

The wet deposition directional patterns for all ions were found to follow closely the precipitation variability in every case. The wet deposition cumulative total of the Ohio Valley/Midwest sector was found to account for approximately 50-70% of the total wet deposition that could be classified into the 48-hour approach trajectories. Wet deposition from the Canadian/Great Lakes sector resulted largely from winter coastal storms in the form of snow or mixed precipitation. Even though ionic concentrations were generally lower for these events, the large values of precipitation sample volume resulted in almost 30% of the total wet deposition at Whiteface Mountain.

These analyses do not suggest that all air masses arriving at Whiteface Mountain display these same characteristics. These figures represent the annual total amounts and directional variability of wet deposition for precipitating events only. The same sectional distribution may not be applicable to dry deposition or special events such as dew, fog, or cloud water.

3.3.2 Illinois (1978)

The same analysis procedure (ARL-ATAD model) was applied to the MAP3S precipitation chemistry for the Illinois site during 1978. Since large pollutant sources for SO_2 , NO_x , etc., lie to the east or southeast of the Illinois station, one might expect to see a significant difference in the deposition pattern or pollution-related ions observed at Whiteface Mountain during the same year.

Figures 36 through 38 depict the distribution of ionic concentration as a function of trajectory approach sector (48-hour back trajectories) for the Illinois site during 1978. Using the same classification criteria described in section 3.3.1, approximately 85% of the precipitation events for the year could be analyzed using the ARL-ATAD model.

The concentrations of sulfate and nitrate, Figure 36, exhibit much more directional uniformity at the Illinois site than at the Whiteface Mountain station. The latter site shows generally higher values for the southwest quadrant. The contribution of snow or mixed precipitation in the northeastern sector is noticeably absent for this midwestern station. The singular data points for the $0-90^\circ$ sectors are not considered statistically significant so that a uniform concentration distribution can be said to exist for Illinois for essentially all approach sectors. The remaining constituents of H^+ , NH_4^+ , Ca^{++} , and Mg^{++} , Figures 37 and 38, display similar uniformity with respect to air mass approach direction.

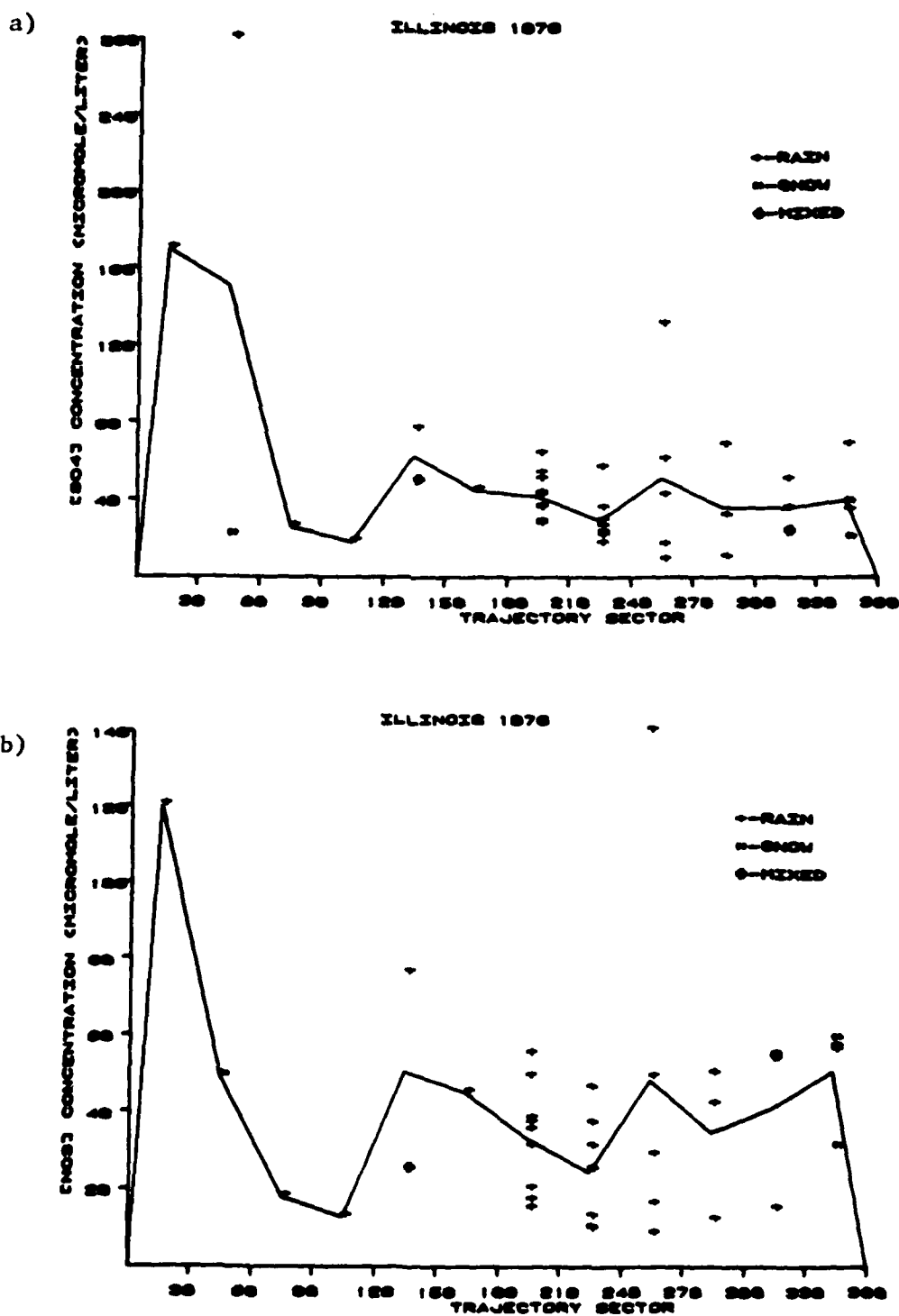


Figure 36. a) Sulfate, and b) Nitrate concentration per 30° trajectory sector for Illinois, 1978.

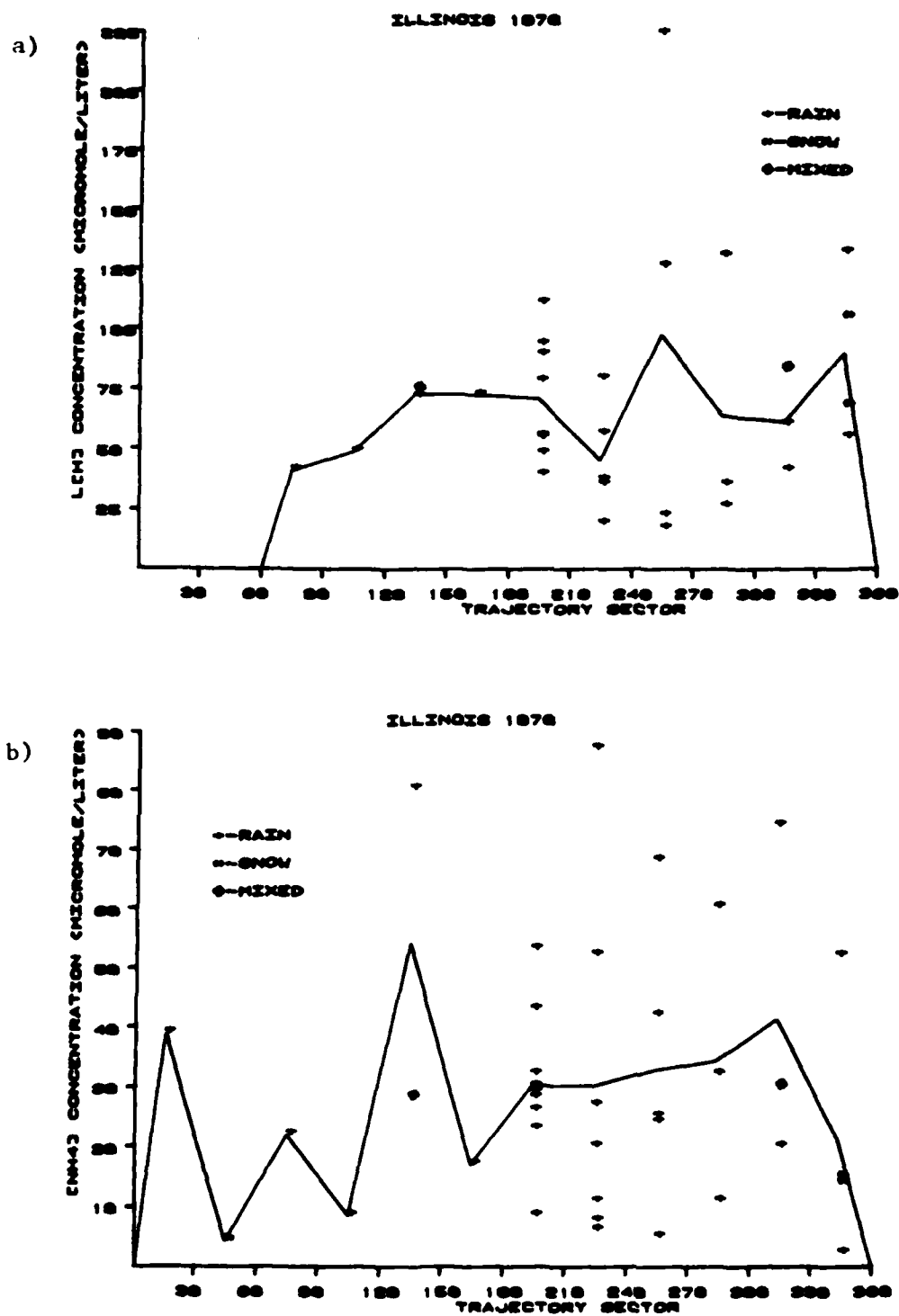


Figure 37. a) Free hydrogen ion, and b) Ammonium ion concentration per 30° trajectory sector for Illinois, 1978.

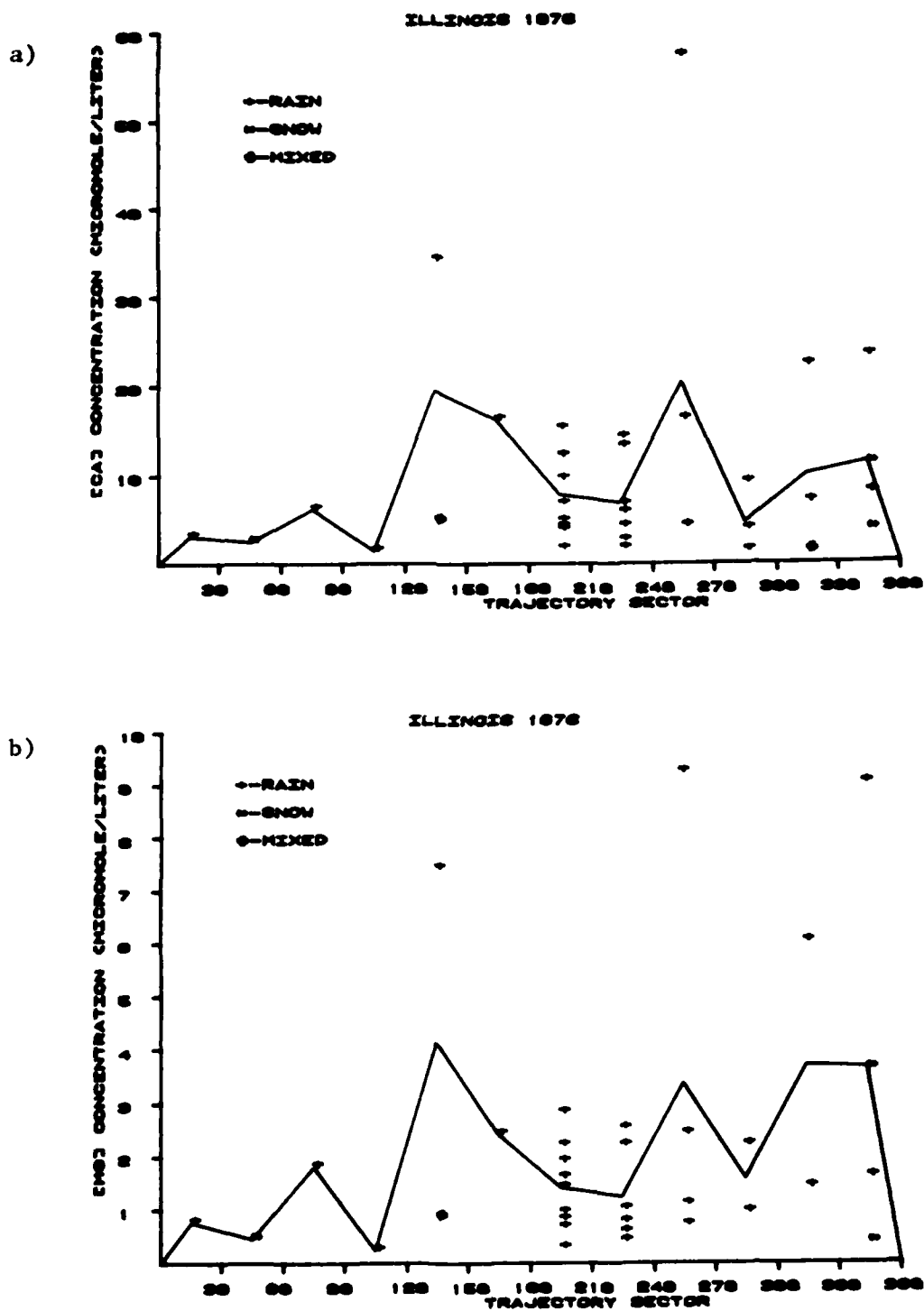


Figure 38. a) Calcium, and b) Magnesium ion concentration per 30° trajectory sector for Illinois, 1978.

The cumulative wet deposition total for these events is plotted in Figures 39 and 40 revealing an entirely different picture. Approximately 70% of the total precipitation for Illinois was found to be associated with the southwest approach sector. This is consistent with synoptic considerations whereby southwesterly flow normally precedes an approaching cyclone system and subsequent deposition events. The remainder of the precipitation was found to be essentially equally distributed over the various sectors with the exception of the 0-30° segment.

Air masses approaching the Illinois site from the southwest were found to deliver about 70% of the total annual precipitation resulting in the deposition of approximately 70% of the major ions (Figures 39b and 40). One can see again that wet deposition of pollution-related ions depends primarily on the precipitation amount.

Trajectory sector analysis may be coupled with regional emission data to investigate the wet deposition pattern at a particular location. The emission data covering the continental United States east of the Mississippi River, the states of Iowa, Minnesota, Arkansas, Missouri, and Louisiana are (in tons/year):

<u>Particulates</u>	<u>SO_x</u>	<u>NO_x</u>	<u>SO_x/NO_x ratio</u>
5.98 x 10 ⁶	2.16 x 10 ⁷	8.21 x 10 ⁶	2.63

For the "Midwest/Ohio Valley" region, covering Indiana, Illinois, Ohio, Kentucky, West Virginia and Pennsylvania alone, the annual emissions are (in tons/year):

<u>SO_x</u>	<u>NO_x</u>	<u>SO_x/NO_x ratio</u>
1.09 x 10 ⁷	3.76 x 10 ⁶	2.90

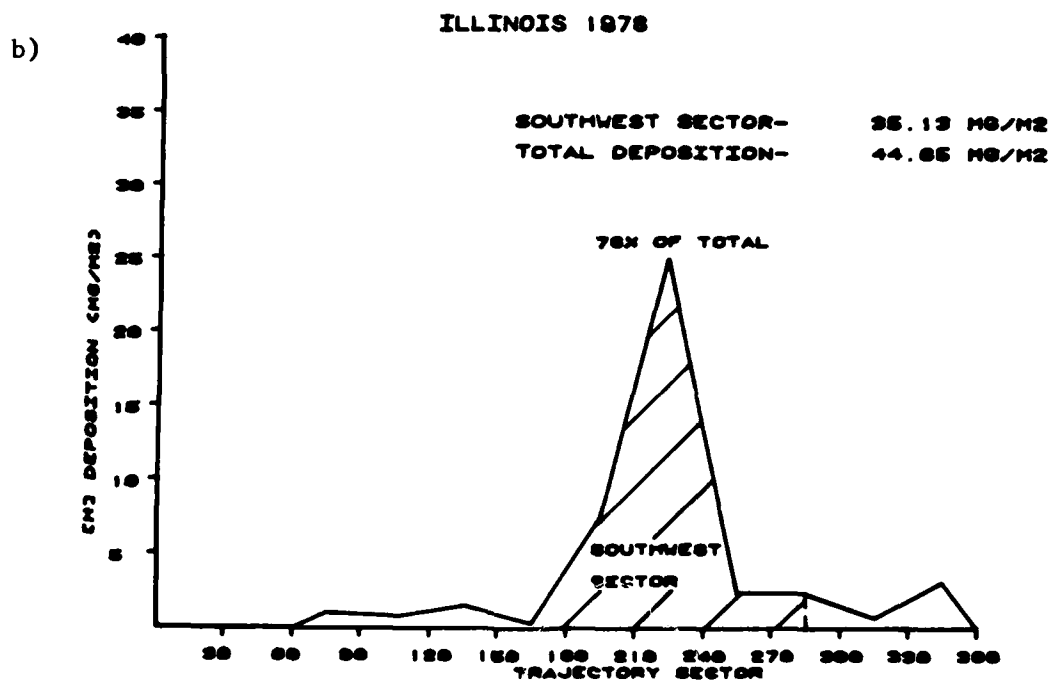
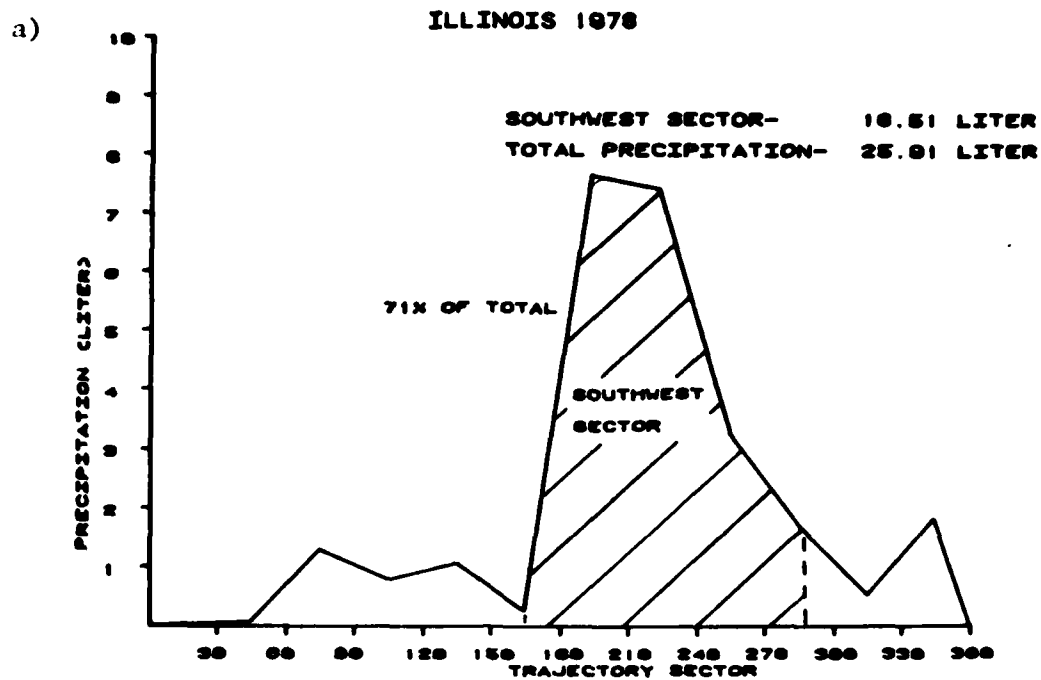


Figure 39. a) Precipitation, and b) Free hydrogen ion deposition per 30° trajectory sector for Illinois, 1978.

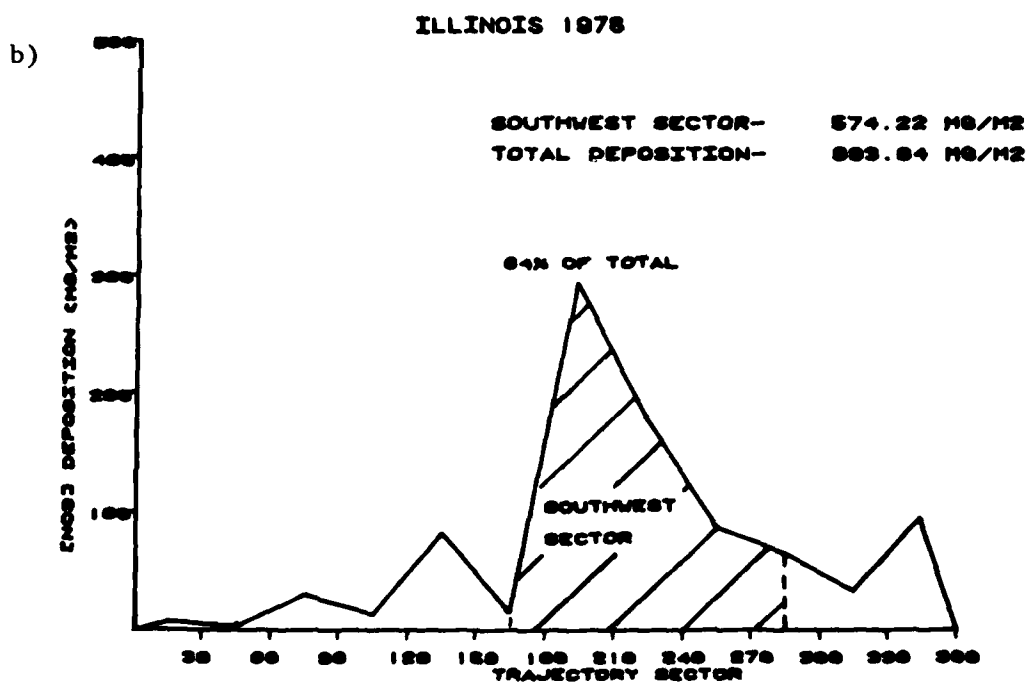
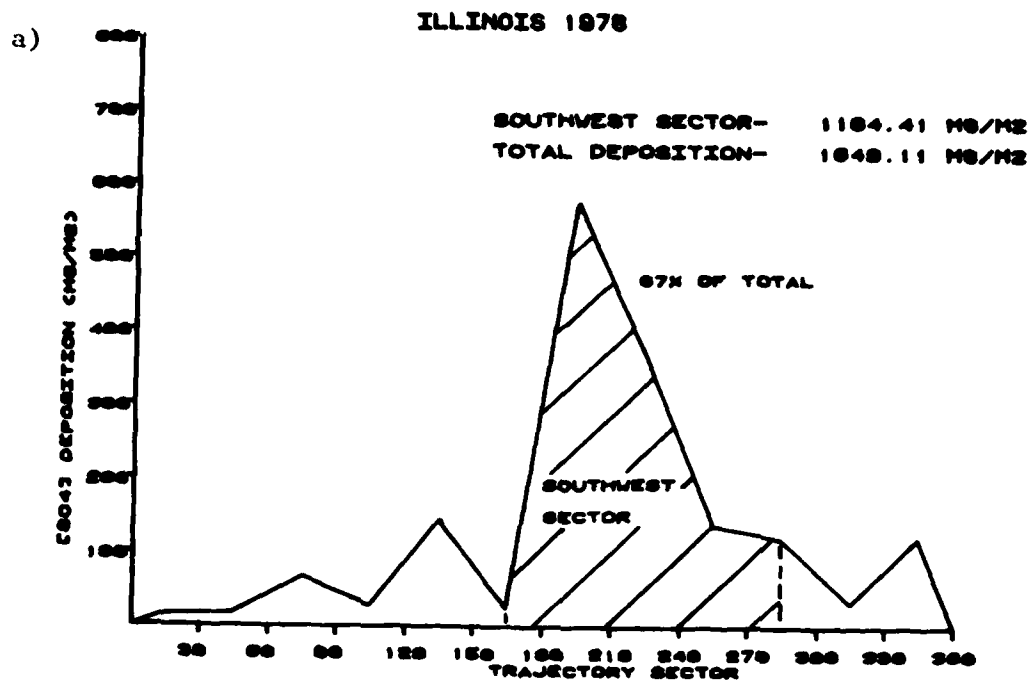


Figure 40. a) Sulfate, and b) Nitrate deposition per 30° trajectory sector for Illinois, 1978.

For the Canadian provinces of Nova Scotia, Newfoundland, Quebec, Ontario, Prince Edward Island and New Brunswick, the annual emissions are (in tons/year):

<u>Particulates</u>	<u>SO_x</u>	<u>NO_x</u>	<u>SO_x/NO_x ratio</u>
2.81 x 10 ⁵	3.01 x 10 ⁶	1.57 x 10 ⁵	19.2

The emissions in the "Midwest/Ohio Valley" region versus the "Canadian/Great Lakes" area are higher by a factor of 3.6 for sulfur components and 24 for nitrogen components.

One might expect to see significant differences in precipitation chemistry as air masses from different regions arrive at a receptor site. The analysis shows:

Whiteface Mountain (1978)

Midwest/Ohio Valley (160°-280° sector)	56% of the annual precipitation delivering
	62% of the annual [H ⁺] deposition
	64% of the annual [SO ₄ ⁼] deposition, and
	65% of the annual [NO ₃ ⁻] deposition
Canadian/Great Lakes (280°-30° sector)	26% of the annual precipitation delivering:
	31% of the annual [H ⁺] deposition
	31% of the annual [SO ₄ ⁼] deposition, and
	28% of the annual [NO ₃ ⁻] deposition

Illinois (1978)

(160°-280° sector)	71% of the annual precipitation delivering:
	78% of the annual [H ⁺] deposition
	67% of the annual [SO ₄ ⁼] deposition, and
	64% of the annual [NO ₃ ⁻] deposition

It is quite apparent that the precipitation volume, more than any other single factor, determines the amount of deposition for the three pollution-related ions, $[H^+]$, $[SO_4^{=}]$ and $[NO_3^-]$. The deposition of ions from "Midwest/Ohio Valley" air and "Great Lakes/Canadian" air does not reflect the very significant differences in emissions that are located in these two regions. The Illinois results further substantiate the above conclusion. There seems to exist no simple, straightforward relationship between emission source(s) for acid precipitation precursor gas(es) and receptors of "acid rain," i.e., $[H^+]$, $[SO_4^{=}]$ and $[NO_3^-]$ ions. The chemical transformation pathway(s) seem to be complex and insensitive to a 48-hour back trajectory analysis presented here and based upon available meteorological and chemical information.

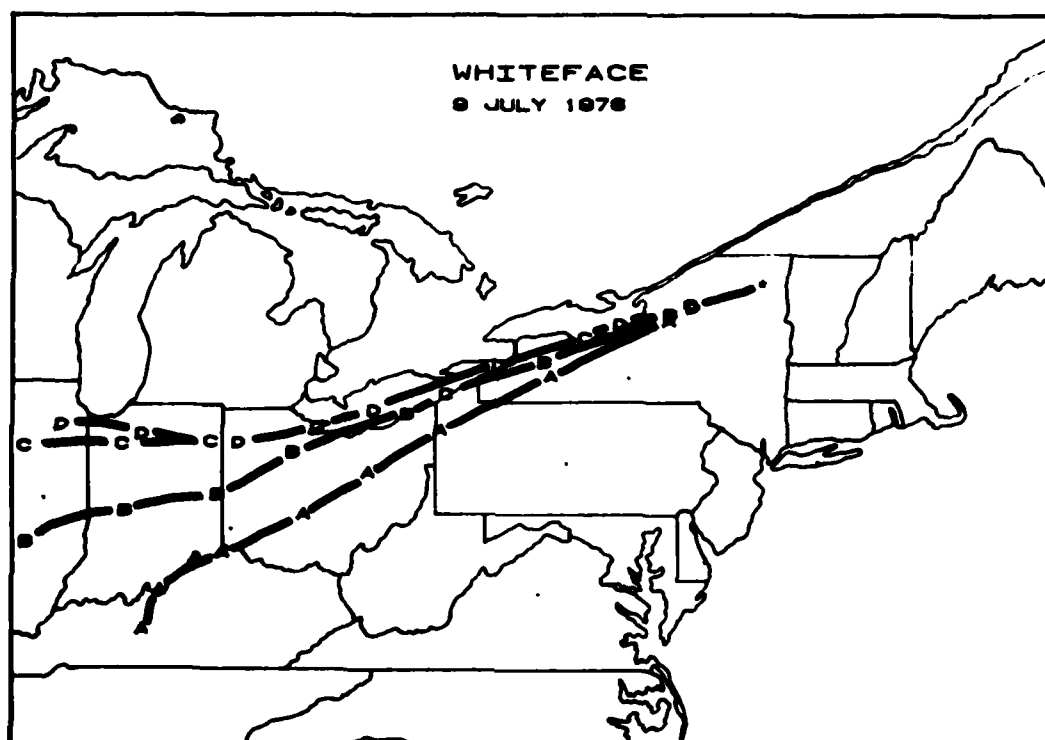
3.4 July 1978 Case Studies

During the month of July 1978, intensive monitoring of air pollution parameters was initiated throughout the Midwest to north-eastern United States. Several air pollution episodes occurred during this month, triggered by the high photochemical potential that coincides with high pressure systems. Precipitation events that follow such anticyclonic events could conceivably lead to rain that is enriched in pollution-related ions ($SO_4^{=}$, NO_3^- , H^+ , etc.). In order to investigate this hypothesis, it is crucial to know the origin of air masses. The MAP3S site at Whiteface Mountain is again selected as the study site in order to see whether air pollution episodes

concentrated in the "Ohio Valley" region and occurring under anti-cyclonic conditions do have an impact on the northeastern United States (Adirondack region) precipitation chemistry.

The July 1978 back trajectories for Whiteface Mountain as developed by the ARL-ATAD model are shown in Figures 41 through 45. Each letter of the trajectory indicates a six hour endpoint whereby the A-trajectory denotes 00Z, the B denotes 06Z, the C denotes 12Z, and the D denotes 18Z. Therefore, relative speed of the air parcels as well as direction is obtainable from these figures. Trajectories which terminate with less than eight endpoints are usually caused by insufficient transport layer depth or lack of usable meteorological upper air data. As mentioned earlier, trajectories were not extrapolated past two days. Included in each figure is the MAP3S collection date, event concentration and deposition of the four major ions, sample volume, and ion ratio. Figure 46 gives the detailed six-hour precipitation totals for Whiteface Mountain for July of 1978 which can be used to weight by volume the trajectories in order to determine the dominant contributor(s) in the case of conflicting or diverse directions. The interval during which precipitation occurred as shown in Figure 46 refers to local standard time, while trajectory calculations are based on Zulu time.

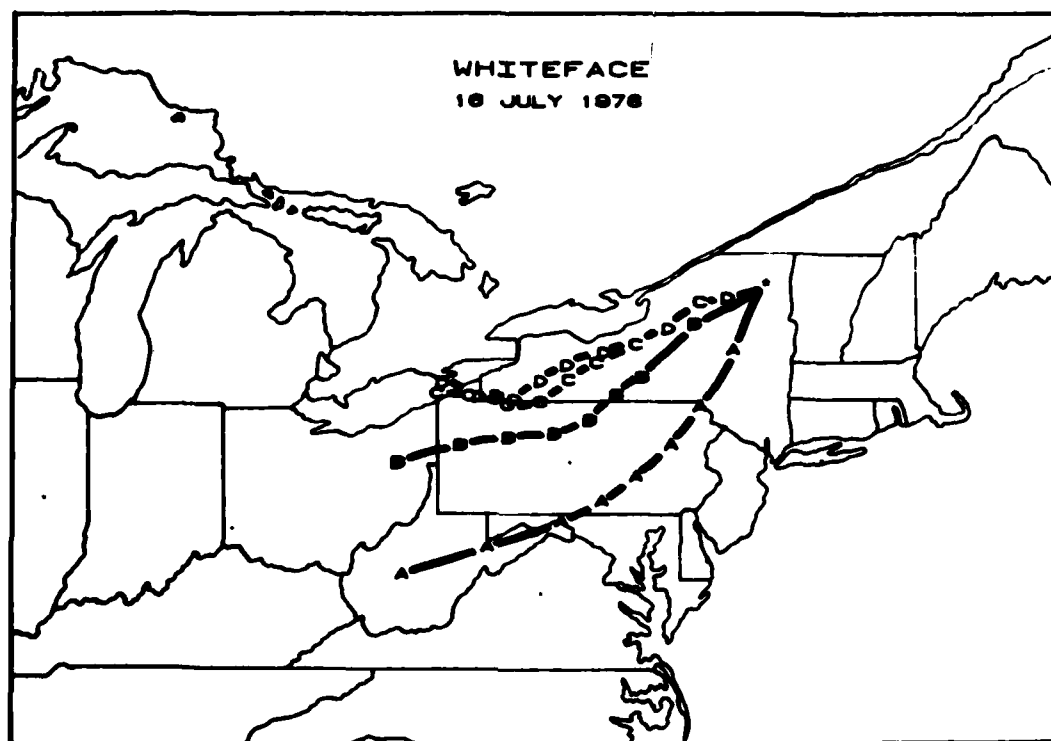
The Sulfate Regional Experiment (SURE) air quality data for July 1978 were used to determine ambient air quality conditions, and in particular to delineate sulfate episodes worthy of examination. Figures 47, 48, 49 and 50 illustrate ambient conditions based on 24-hour HIVOL sampling and rainfall for Whiteface and Ithaca. There were



MAP3S Event - 11 July 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	110	49	27	23
Deposition (mg/m^2)	0.81	35	12	3.1
Sample volume - 362 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.01$				

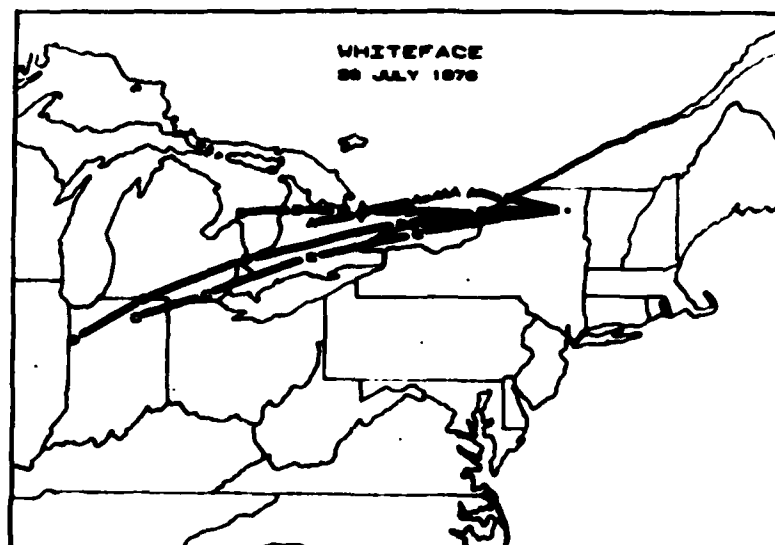
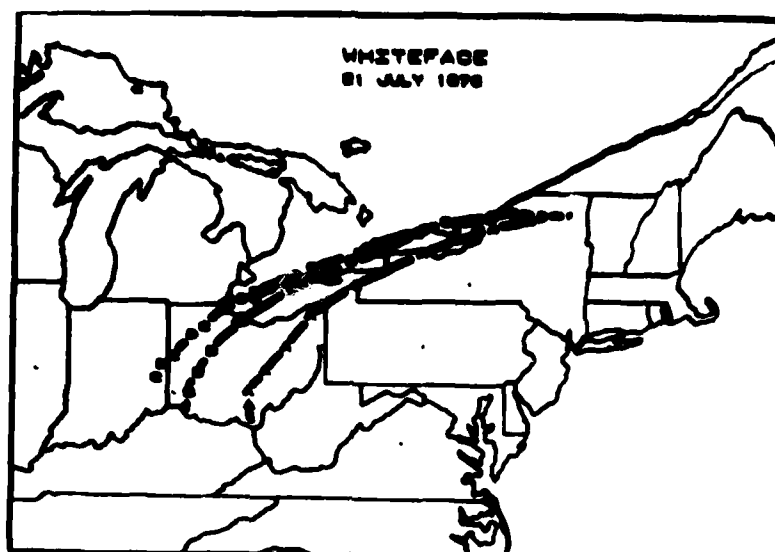
Figure 41. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 11 July, 1978.



MAP3S Event - 18 July 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	150	97	82	60
Deposition (mg/m^2)	0.26	16	8	1.9
Sample volume - 84 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.76$				

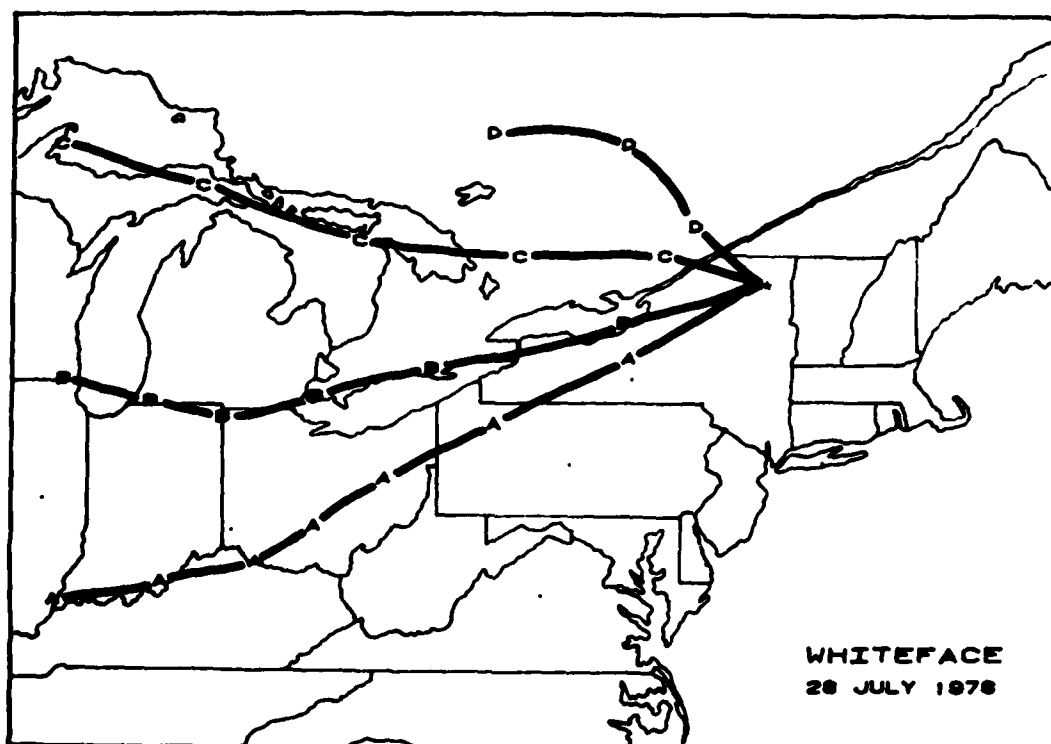
Figure 42. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 18 July, 1978.



MAP3S Event - 24 July 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	150	88	45	54
Deposition (mg/m^2)	0.81	45	14	5.2
Sample volume - 264 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.92$				

Figure 43. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 24 July, 1978.



MAP3S Event - 28 July 1978

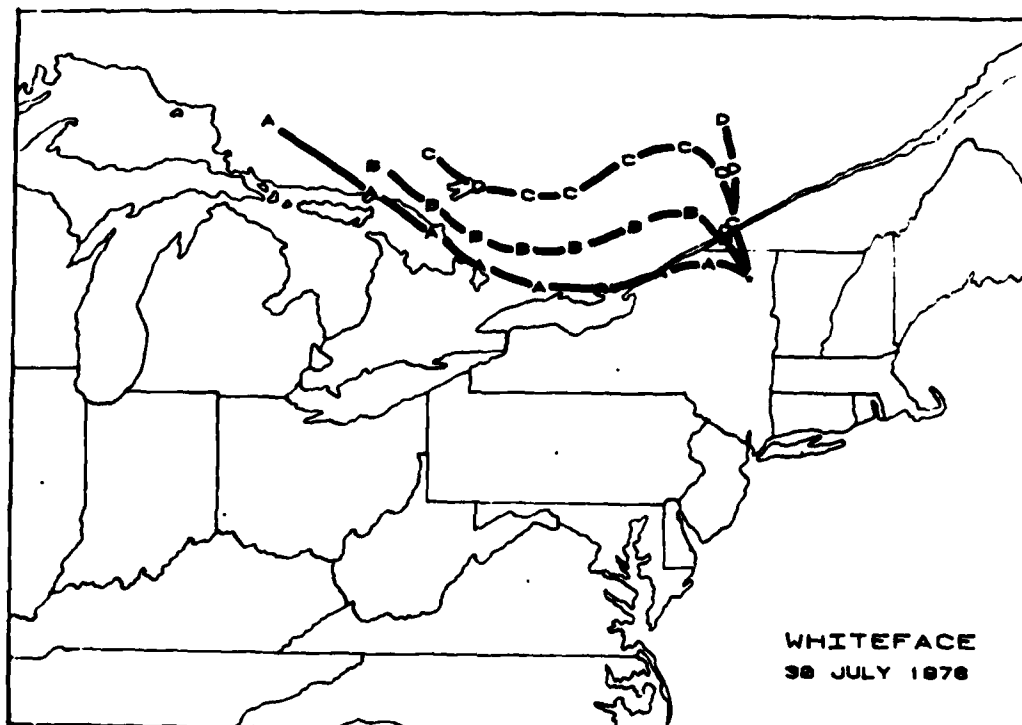
	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	98	58	64	19
Deposition (mg/m^2)	0.9	52	36	3.3

Sample volume - 450 ml

$$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.65$$

(Note: total cation/total anion = 0.84)

Figure 44. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 28 July, 1978.



MAP3S Event - 31 July 1978

	<u>$[H^+]$</u>	<u>$[SO_4^{=}]$</u>	<u>$[NO_3^-]$</u>	<u>$[NH_4^+]$</u>
Concentration ($\mu\text{mole/liter}$)	26	10	8.9	3.1
Deposition (ng/m^2)	0.33	12	6.8	0.7
Sample volume - 623 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.01$				

Figure 45. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 31 July, 1978.

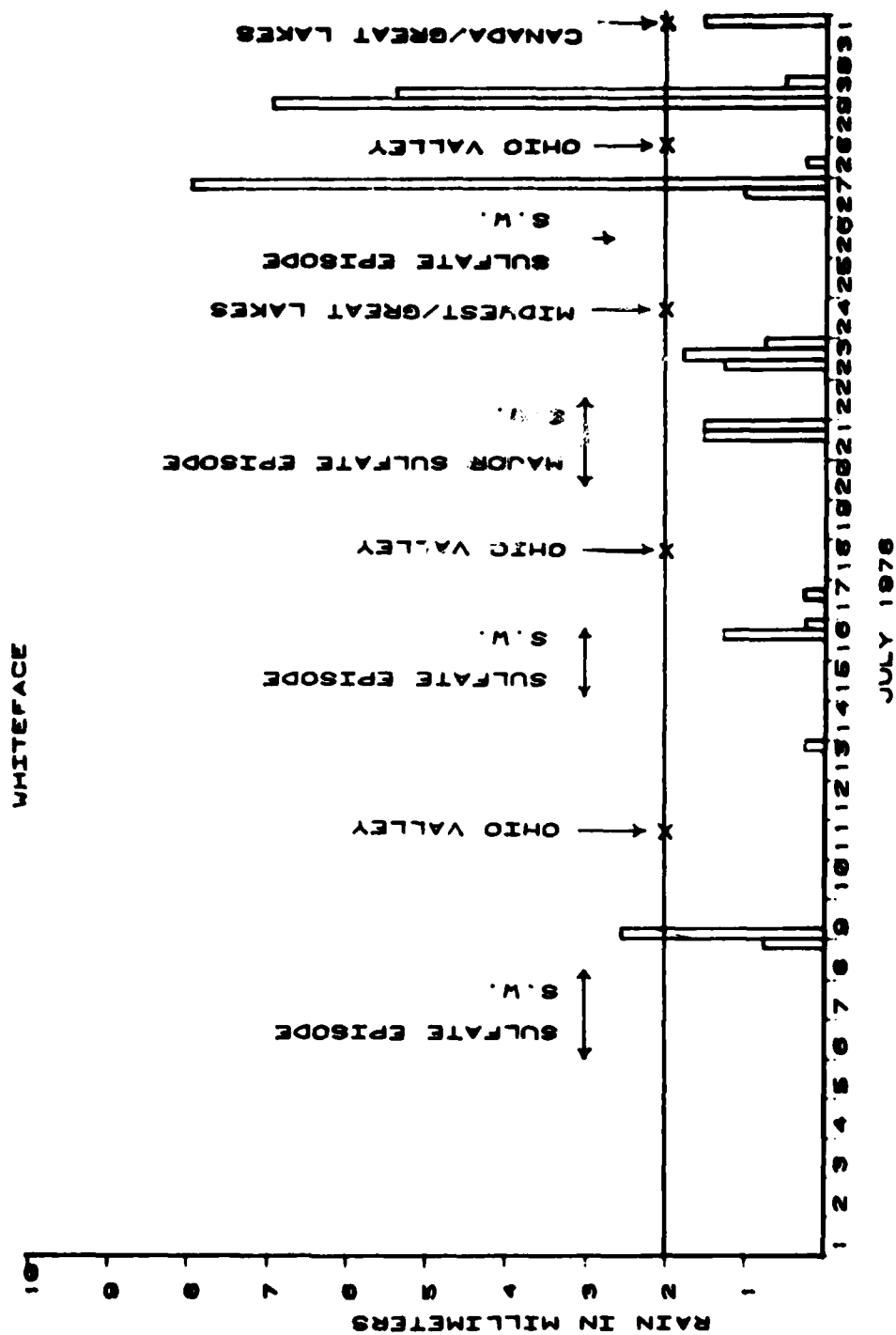


Figure 46. Six hour precipitation and event classifications for Whiteface, July 1978.

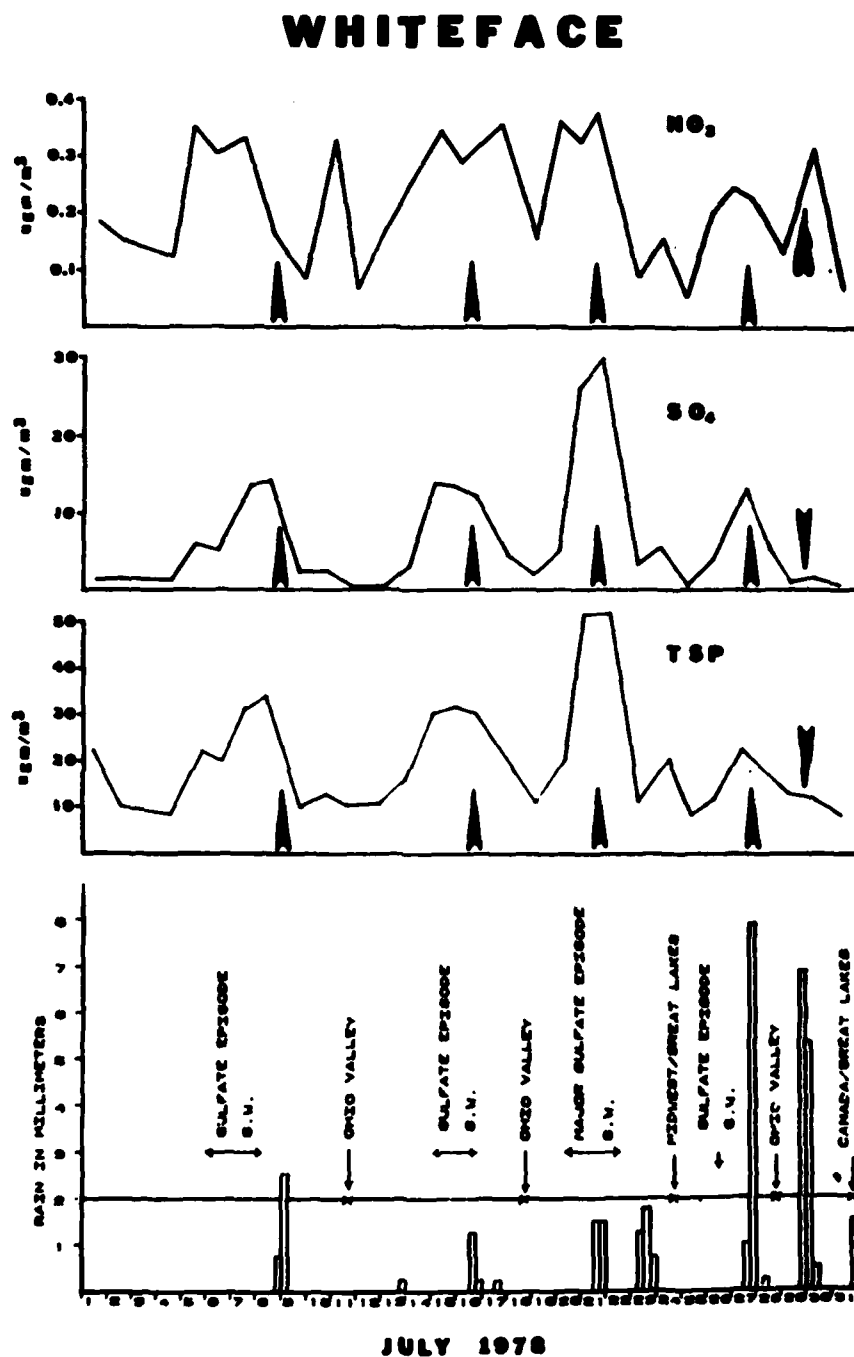


Figure 47. SURE air quality data and 6-hour rainfall totals for Whiteface, July 1978.

WHITEFACE AIR QUALITY DATA JULY 1978

Date	TSP	NO ₃	μ mg/m ³	
			SO ₄	SO ₂
1	22.934	0.187	1.464	16.921
2	10.756	0.163	1.746	18.013
3	--	--	--	19.432
4	9.315	0.120	1.086	18.340
5	23.454	0.341	6.130	21.178
6	20.623	0.316	5.301	21.506
7	32.780	0.333	13.770	28.618
8	35.301	0.183	15.889	--
9	11.966	0.097	2.445	--
10	13.790	0.316	3.315	--
11*	10.272	0.080	0.909	--
12	11.739	0.176	0.958	--
13	17.064	0.239	3.745	--
14	31.642	0.322	14.100	--
15	32.010	0.293	13.925	--
16	30.587	0.320	12.206	--
17	19.776	0.369	6.334	--
18*	13.462	0.176	2.316	--
19	22.108	0.352	6.523	--
20	53.124	0.309	25.936	--
21	53.180	0.356	29.347	--
22	13.206	0.099	3.634	--
23	22.222	0.153	7.229	--
24*	10.821	0.088	0.671	--
25	14.359	0.205	3.339	--
26	26.878	0.229	12.045	--
27	19.255	0.222	6.700	--
28*	14.865	0.116	0.920	--
29	13.963	0.290	1.390	--
30	9.714	0.084	0.655	--
31*	--	--	--	--

*MAP3S Event

Figure 48. 24-hour HIVOL air quality data for Whiteface, July, 1978 as measured by the SURE network.

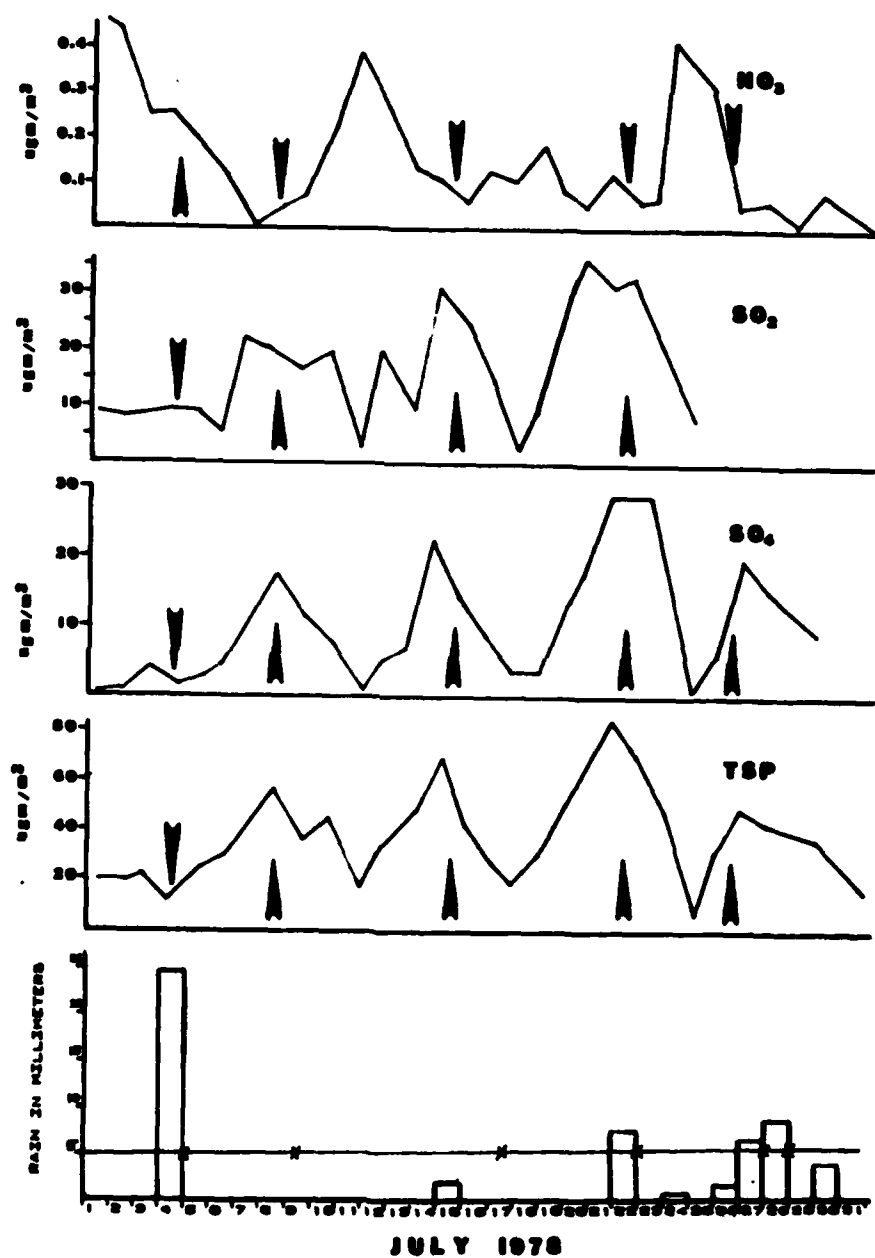
ITHACA

Figure 49. SURE air quality data and daily rainfall for Ithaca, July 1978.

ITHACA AIR QUALITY DATA JULY 1978

Date	TSP	Cl ⁻	NH ₄ ⁺	micro gram/m ³				Rainfall inch	(μ mole/l) MAP3S			
				NO ₃ ⁻	SO ₄ ⁻	SO ₂			L[H ⁺]	SO ₄ ⁻	NO ₃ ⁻	NH ₄ ⁺
1	19.3	--	--	0.477	1.792	8.813		--				
2	19.8	--	--	0.434	1.439	7.423		--				
3	21.4	--	--	0.246	4.442	8.952		--				
4*	11.4	--	--	0.268	2.212	9.061		.96	66	16	22	3.5
5	22.5	--	--	0.192	3.456	8.842		--				
6	29.5	--	--	0.133	4.826	5.677		--				
7	--	--	--	0.002	--	22.487		--				
8	56.2	--	--	0.057	18.915	21.833		--				
9*	38.7	--	--	0.073	12.572	18.668		--	169	74	37	28
10	44.7	--	--	0.213	9.020	21.178		--				
11	17.5	--	--	0.399	1.953	4.803		--				
12	33.6	--	--	0.274	5.061	21.615		--				
13	45.0	--	--	0.177	7.831	10.644		--				
14	68.3	--	--	0.128	23.620	31.986		--				
15	44.7	--	--	0.087	16.830	25.872		.12				
16	29.8	--	--	0.187	9.234	14.082		--				
17*	20.5	0.005	0.221	0.110	4.479	3.930		--	129	58	26	23
18	30.1	0.005	0.171	0.192	4.479	11.135		--				
19	--	--	--	0.100	15.362	25.982		--				
20	62.1	0.005	4.416	0.070	18.785	36.134		--				
21	85.3	0.021	5.001	0.113	28.018	32.465		--				
22*	65.3	0.033	7.616	0.063	28.817	33.296		.35	170	63	3.5	.18
23	45.0	0.005	3.939	0.073	16.902	24.890		--				
24	8.1	0.052	0.012	0.401	1.968	8.187		.02				
25	27.4	--	--	0.318	5.186	--		--				
26	46.6	--	--	0.049	20.159	--		.07				
27*	41.8	--	--	0.061	18.003	--		.30	200	87	57	34
28*	--	--	--	0.001	--	--		.36	112	42	35	27
29	30.6	--	--	0.096	10.076	--		--				
30	--	--	--	--	--	--		.15				
31	12.7	--	--	0.002	--	--		--				

*MAP3S Event

Figure 50. 24-hour HIVOL air quality data for Ithaca, July 1978, as measured by the SURE network.

essentially four sulfate episodes during July 1978 that are reflected in the total suspended particulates, SO_4 (aerosol) and SO_2 . The aerosol nitrate concentration demonstrates no significant trend or, in the case of Ithaca, exhibits a negative correlation with concentration values of the other aerosol constituents.

The cleansing mechanisms of rainout and washout and/or the change of air mass (anti-cyclonic versus cyclonic) are apparent, causing a significant decrease in total suspended particulates and in other pollution-related materials. The early part of July for Ithaca is somewhat confusing in this respect, since the National Climatic Center data indicate no rainfall between 5 July and 9 July, but a MAP3S collection accounted for 2.65 mm, suggesting at least some precipitation activity during this period. Localized summertime convective showers may be used to explain this discrepancy. Rainfall amounts in Figure 49 are taken from National Climatic Center Daily Precipitation Summaries.

With this information, the individual precipitation events and preceding ambient conditions at Whiteface Mountain can be classified

as follows:	<u>Rain Event at WFM</u>	<u>MAP3S Collection</u>	<u>Origin of Air Mass/Characterization</u>
	7/8	7/11	"Ohio Valley" preceded by sulfate episode
	7/16	7/18	"Ohio Valley" preceded by sulfate episode
	7/21 and 7/23	7/24	"Midwest/Great Lakes" preceded by a major sulfate episode
	7/27	7/28	"Ohio Valley" preceded by a sulfate episode
	7/29	7/31	"Canada/Great Lakes"

There is a striking difference in concentration values between the air masses arriving at Whiteface Mountain from the "Midwest" to "Ohio Valley" region and the "Canada" to "Great Lakes" region. The intensity weighted $[SO_4^{=}]$, $[NO_3^{-}]$, and $[H^{+}]$ concentration for these two different regions are:

	Concentration			MAP3S Events
	H^{+} $\mu\text{mole/L}$	$SO_4^{=}$ $\mu\text{mole/L}$	NO_3^{-} $\mu\text{mole/L}$	
WFM	$\overline{146}$	$\overline{65}$	$\overline{50}$	Combined July 11, 18, 24 and 28 MAP3S events (The bar indicates the mean)
	46	10	8.9	Canada/Great Lakes
ITH	$\overline{138}$	$\overline{55}$	$\overline{34}$	Combined July 9, 17, 22, 27, 28 (The bar indicates the mean)
	46	16	22	July 4 "Canadian" air
	25	9.4	6.7	August 7 events
PEN	$\overline{170}$	$\overline{71}$	$\overline{45}$	Combined July 7, 11, 15, 24, 28, 30 events (The bar indicates the mean)
	71	25	13	July 4 event "Canadian" air

Concentration ($\mu\text{mole/L}$) of pollutant material is one way of characterizing the impact of precipitation on a region. Deposition (mg/m^2 or $\mu\text{equiv/m}^2$) is another equally, if not more, important parameter. For July 1978, the following deposition picture emerges for the "Midwest/Ohio Valley" versus "Canada/Great Lakes" region:

	Deposition			MAP3S Events
	H (mg/m ²)	SO ₄ (mg/m ²)	NO ₃ (mg/m ²)	
WFM	0.61 per event 2.44 total for July 78	28.4 per event 113.6 total for July 78	11.7 per event 46.8 total for July 78	Combined July 11, 18 and 24 and 28 Midwest/Ohio Valley (The bar refers to the mean)
	1.58 or 24% of total July	12.2 11% of total	6.8 15% of total	July 31 event Canada/Great Lakes
ITH	2.18 per event 10.90 total for July 78	84.3 per event 241.5 total	31.2 per event 156 total	Combined July 9, 17, 22, 27, 28 Midwest/Ohio Valley (The bar refers to the mean)
	1.29 or 12% of total July 78	43.3 or 18% of total	37.2 or 24% of total	July 4 Canadian air
PEN	0.95 per event 4.76 total for July 78	38.4 per event 192 total	15.2 per event 76 total	Combined July 7, 11, 15, 24, 28, 30 Midwest/Ohio Valley (The bar refers to the mean)
	1.83 39% of total July	62 or 32% of total July	20 or 26% of total	July 4 Canadian air

It can be summarized that the impact of precipitation in July of 1978 originating from the "Great Lakes/Canadian" sector is significantly lower than the impact caused by "Midwest/Ohio Valley" air in regard to the "ion concentration," but comparable in regard to "ion deposition per event." There have been four to five times more events during July 1978 involving air masses from the "Midwest/Ohio Valley." Accordingly, the percent contribution of the precipitation from air masses passing over the Canadian/Great Lakes region is appreciably lower. For example, during July of 1978, 76% of the hydrogen ion, 89% of the sulfate ion and 85% of the nitrate ion were

deposited at Whiteface Mountain from air mass systems that had previously passed over the Midwest/Ohio Valley region. Surprisingly enough, however, a much lower fraction, namely 61% of the hydrogen ion, 68% of the sulfate ion and 75% of the nitrate ions had been deposited at Penn State from similar air masses.

3.5 January 1978 Case Studies

As noted earlier, there exists a seasonal variation in the concentration and deposition of many ions in the northeastern United States. With the exception of nitrate, the major ions exhibit a distinct summer maximum. In this context, case study comparisons between different seasons may be misleading if no consideration is given to air mass trajectories. It was found useful to examine concentration and deposition during the winter months since a more uniform distribution of frequency per approach sector exists for trajectories arriving at Whiteface Mountain. The dominant storms during January 1978 were from rapidly intensifying coastal storms which were responsible for the northerly component of many of the individual events. Figure 51 shows the percentage of occurrence of three-hour trajectory endpoints per square degree latitude and longitude for January and July 1978. While not an absolute measure of the passage of a trajectory over a particular point, it does nevertheless provide insight into the seasonal climatology of air masses arriving in the Adirondacks. The higher frequency of occurrence for trajectories passing over the Midwest/Ohio Valley area, coupled with the increased solar radiation for the summer months, may lead to the summer maximum in ion concentration and ion deposition.

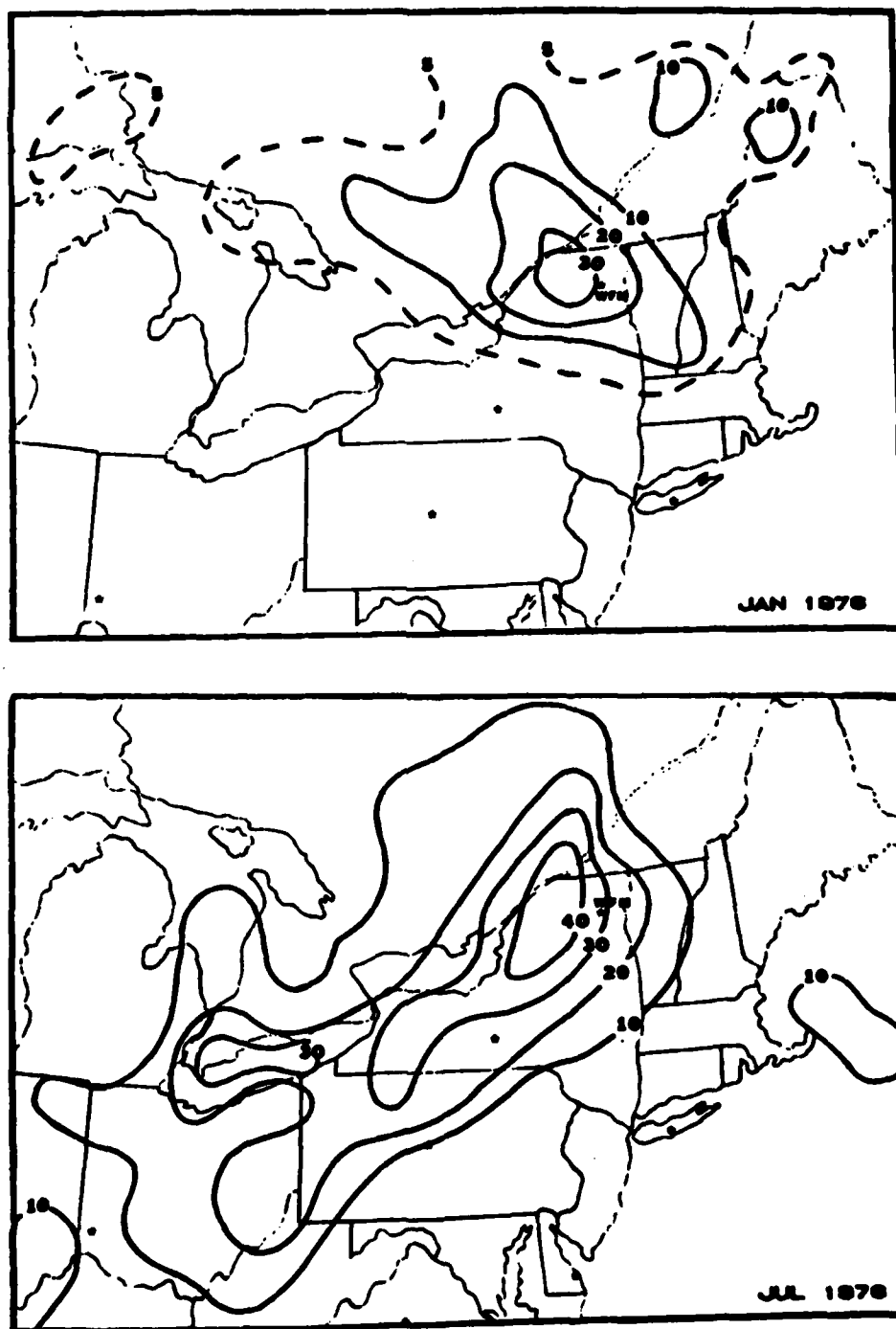
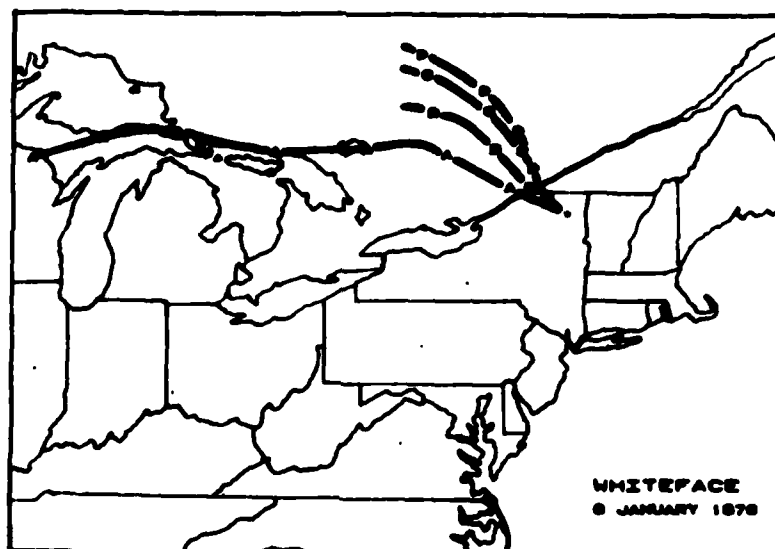
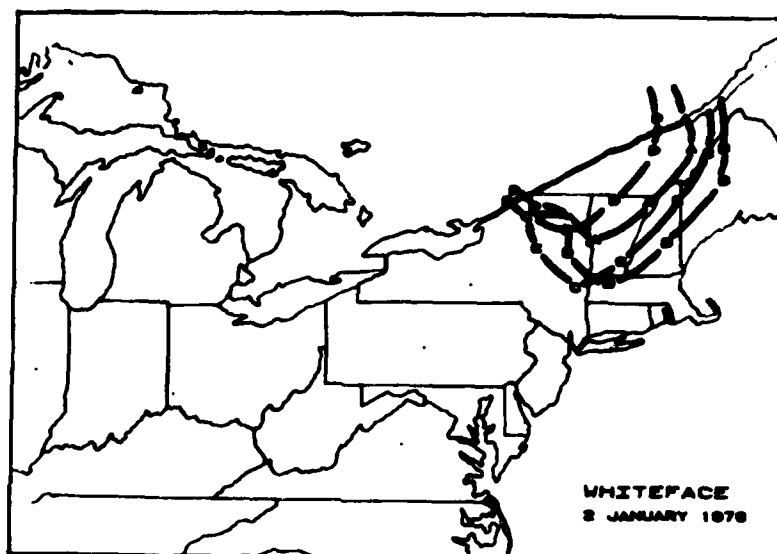


Figure 51. Three-hour trajectory endpoint percent of occurrence per square longitude and latitude for Whiteface, January and July 1978.

Therefore, in order to examine variability within the winter season, precipitation chemistry for the major ions was matched with corresponding air mass trajectories for January 1978, as shown in Figures 52 through 56. Figure 57 gives the six-hour precipitation amounts, MAP3S collection and other general classification of each event. The concentrations are relatively low for each event, with January 13 and 19 being comparable to the extremely "clean" precipitation of Hurricanes David and Frederic (to be discussed later). This is due in part to the large precipitation amounts which are comparable in magnitude to those measured during the hurricanes.

The depositions, however, are in the normal range. It should be noted that, contrary to the summer season, nitrate deposition is comparable to that of sulfate deposition.

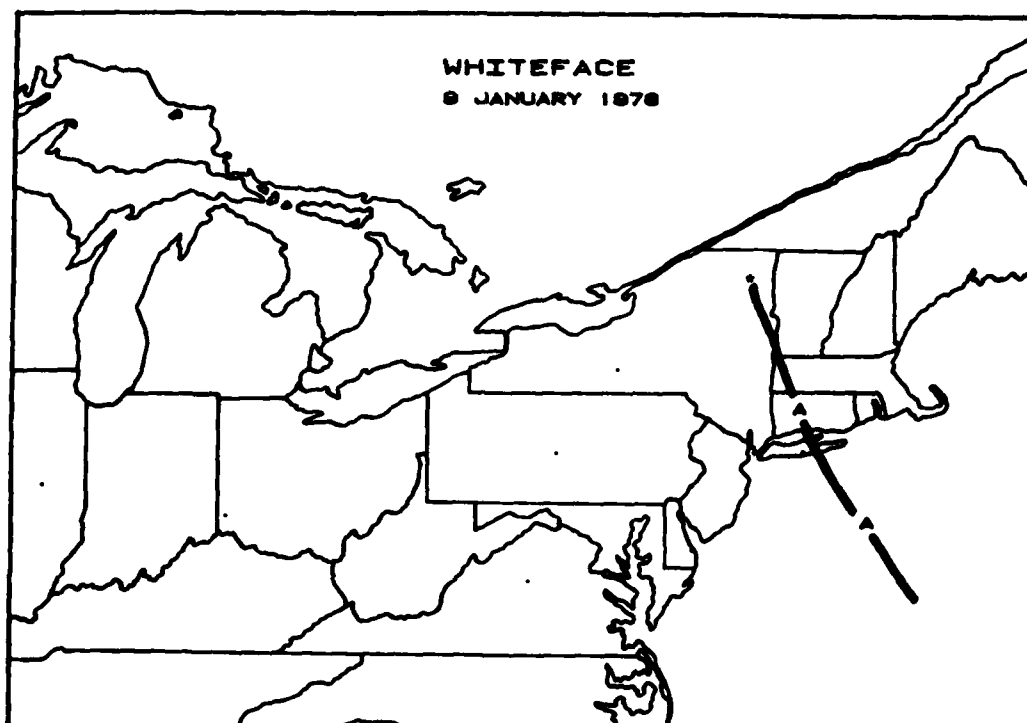
Unfortunately, the January 25, 26, and 27, 1978 events were not separated, although the air trajectories originate from two entirely different regions. Hence, it is impossible to separate for Whiteface Mountain the impact of air masses passing over the Ohio Valley region from that caused by air masses from the Canadian sector. Therefore, in order to achieve this goal, the Ithaca January 1978 data have been analyzed. Figures 58 through 63 show the trajectories calculated for every precipitation event and ending at Ithaca. Again, the pre-dominant flow is from the Great Lakes-to-northeastern Canada sector and the very low concentration values seem to reflect this situation. The deposition values for January 1978 at Ithaca are again moderate



MAP3S Event - 7 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	110	15	91	20
Deposition (mg/m^2)	0.81	11	42	2.6
Sample volume - 260 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.07$				

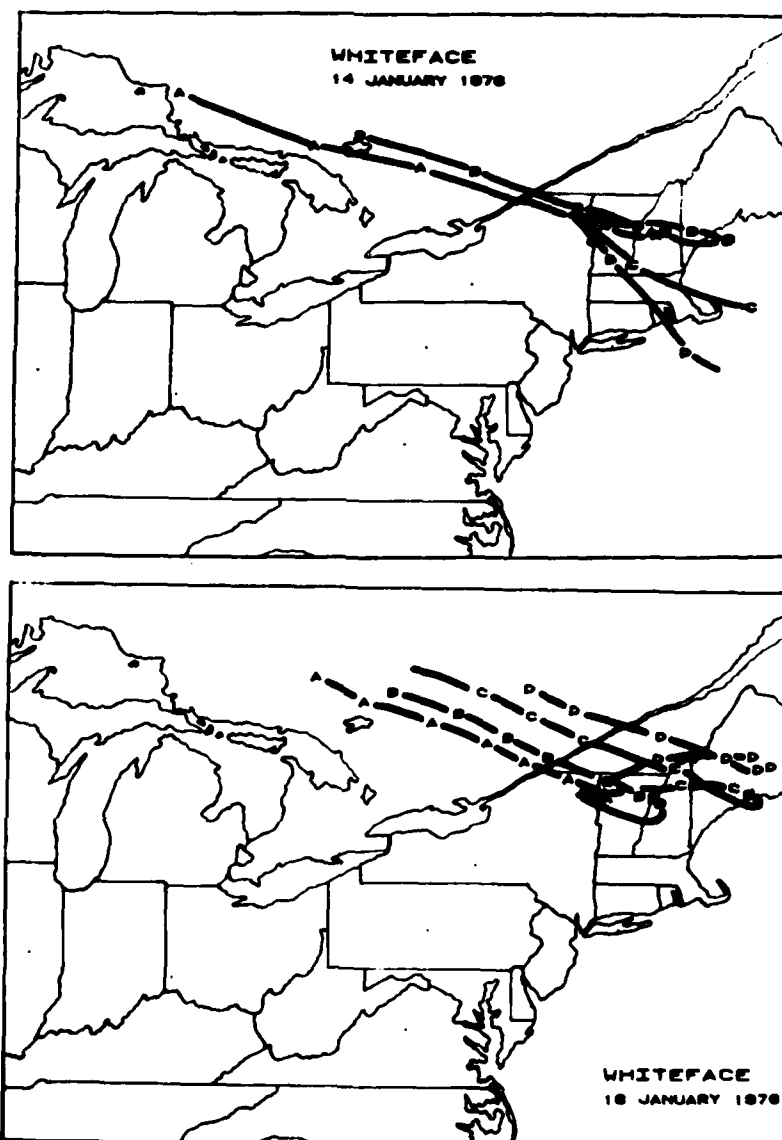
Figure 52. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 7 January, 1978.



MAP3S Event - 13 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	14	4.7	5.8	0.4
Deposition (mg/m^2)	0.44	17.5	11.4	0.3
Sample volume - 1550 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.95$				

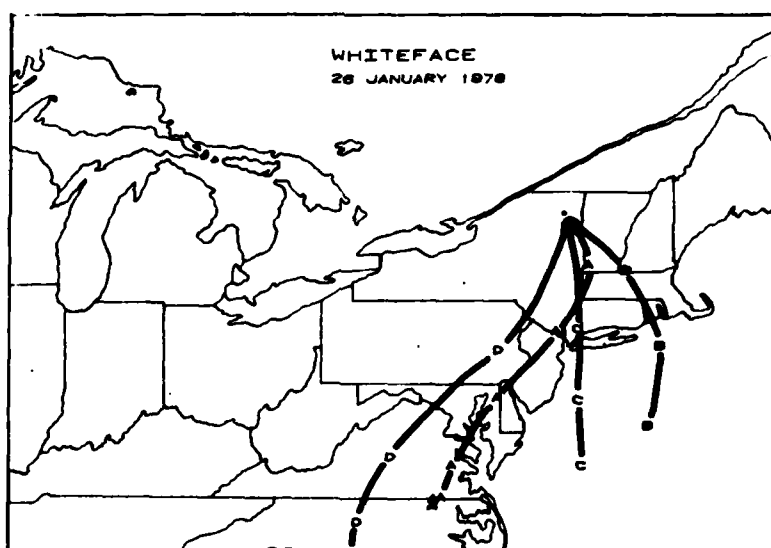
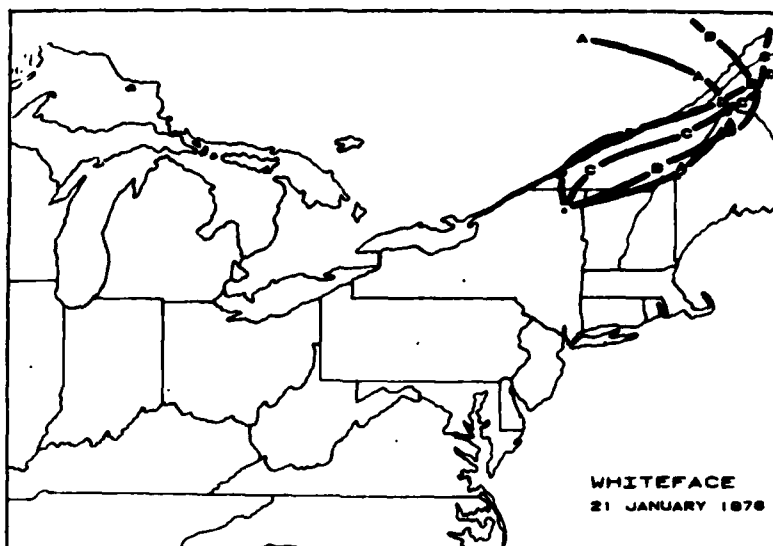
Figure 53. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 13 January, 1978.



MAP3S Event - 19 January 1978

	$[H^+]$	$[SO_4^{2-}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	13	1.9	2.2	0.4
Deposition (mg/m^2)	0.39	6.7	6.1	0.2
Sample volume - 1470 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{2-}] + [NO_3^-] = 2.23$				

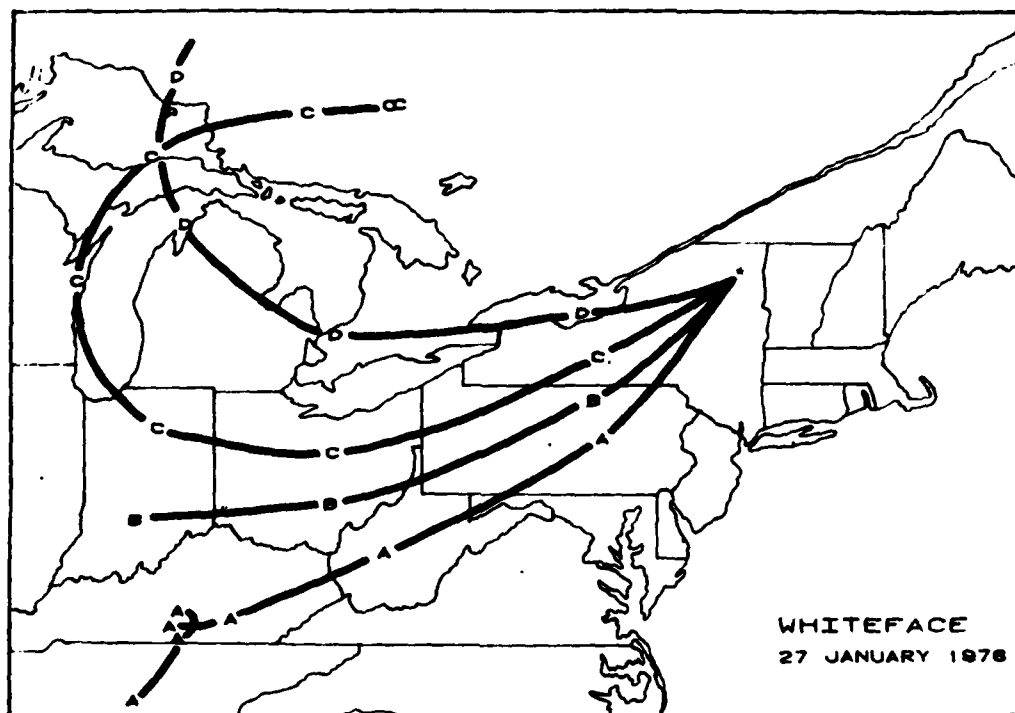
Figure 54. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 19 January, 1978.



MAP3S Event - 26 January 1978

	<u>$[H^+]$</u>	<u>$[SO_4^{=}]$</u>	<u>$[NO_3^-]$</u>	<u>$[NH_4^+]$</u>
Concentration ($\mu\text{mole/liter}$)	30	8.4	12	1.1
Deposition (mg/m^2)	0.89	29.5	26	0.6
Sample volume - 1460 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.08$				

Figure 55. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 26 January, 1978.



MAP3S Event - 31 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	41	37	27	19
Deposition (mg/m^2)	0.20	21	10	1.6
Sample volume - 235 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.59$				

Figure 56. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Whiteface event of 31 January, 1978.

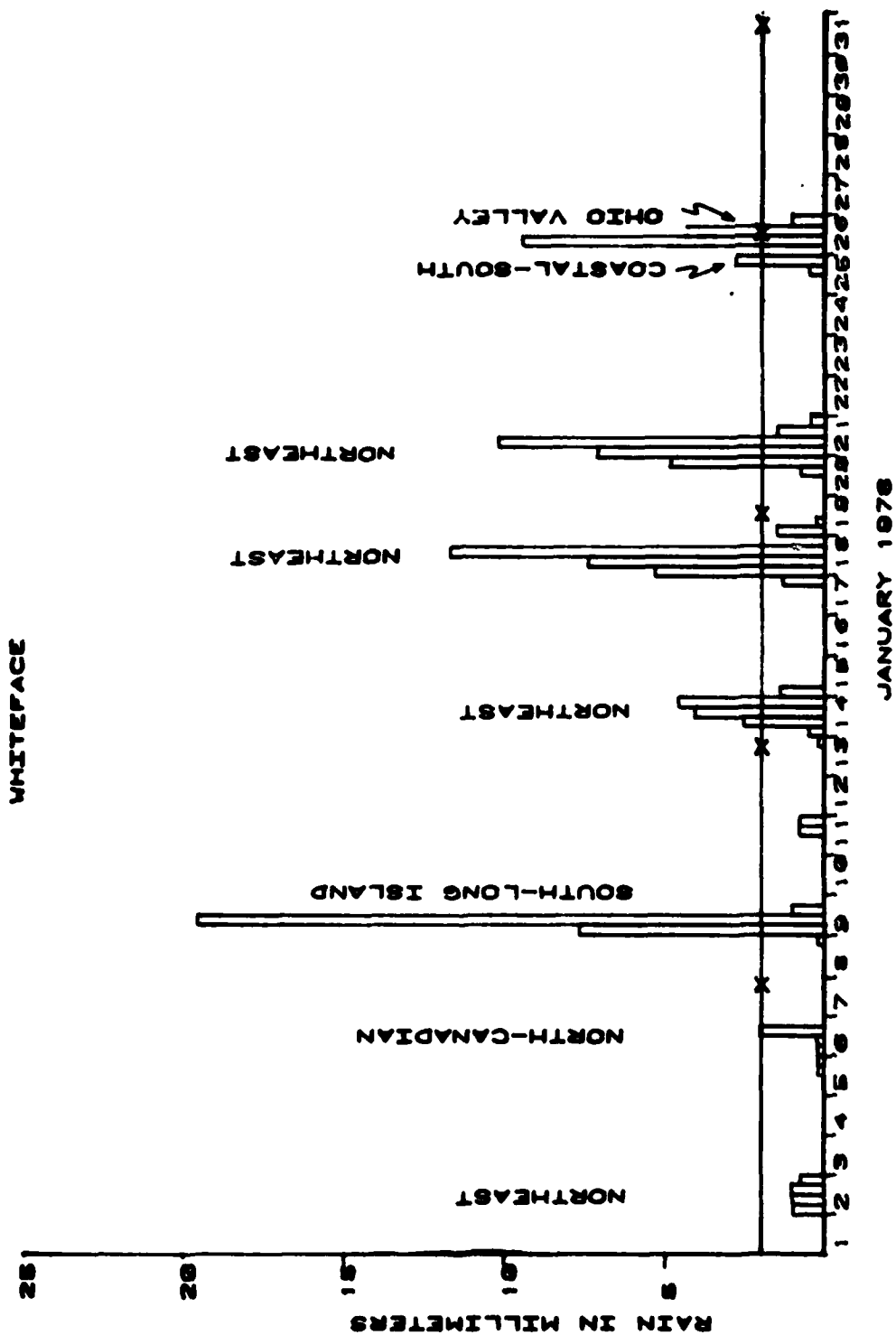
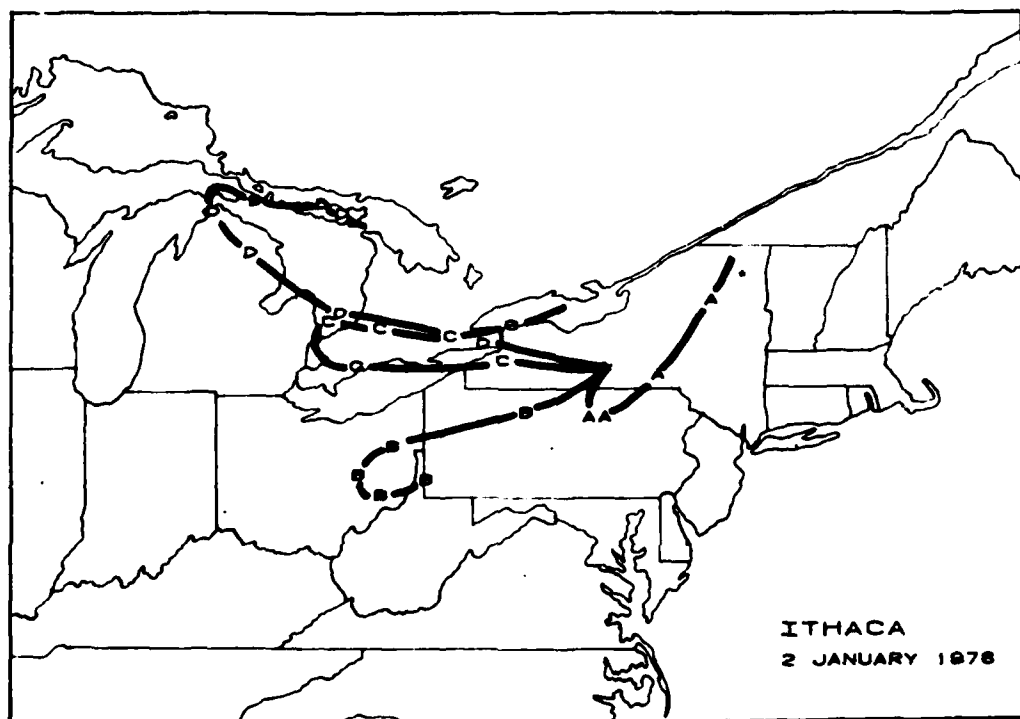


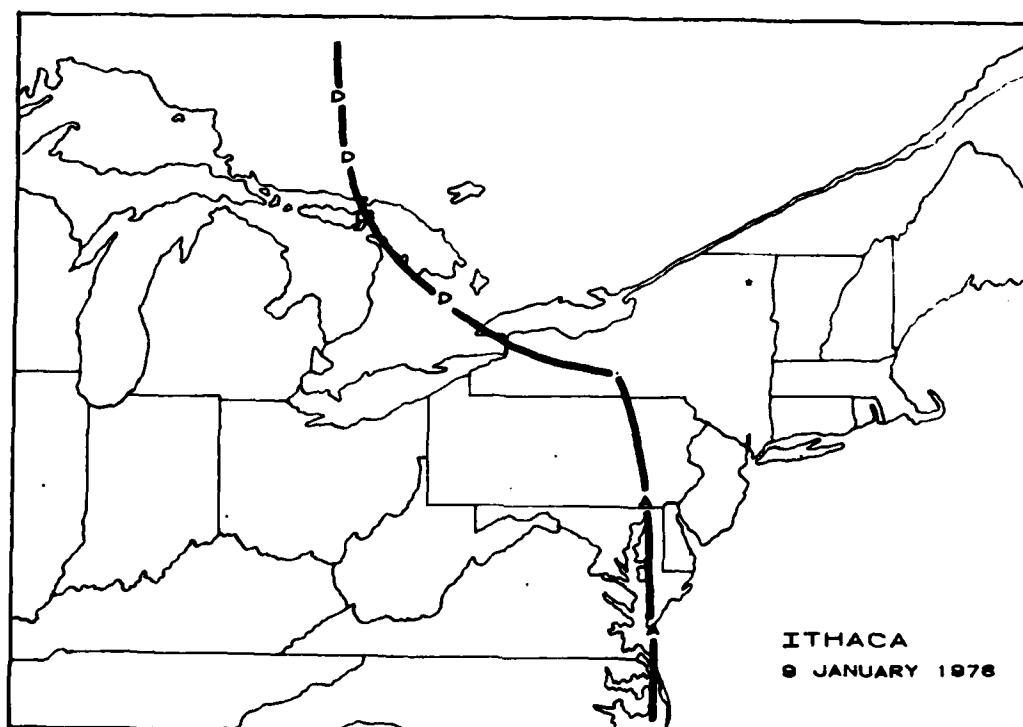
Figure 57. Six-hour precipitation totals and event classification for Whiteface, January 1978.



MAP3S Event - 3 January 1978

	<u>$[H^+]$</u>	<u>$[SO_4^{=}]$</u>	<u>$[NO_3^-]$</u>	<u>$[NH_4^+]$</u>
Concentration ($\mu\text{mole/liter}$)	66	19	55	9.2
Deposition (mg/m^2)	0.34	9.7	18	0.9
Sample volume - 260 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.81$				

Figure 58. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 3 January, 1978.



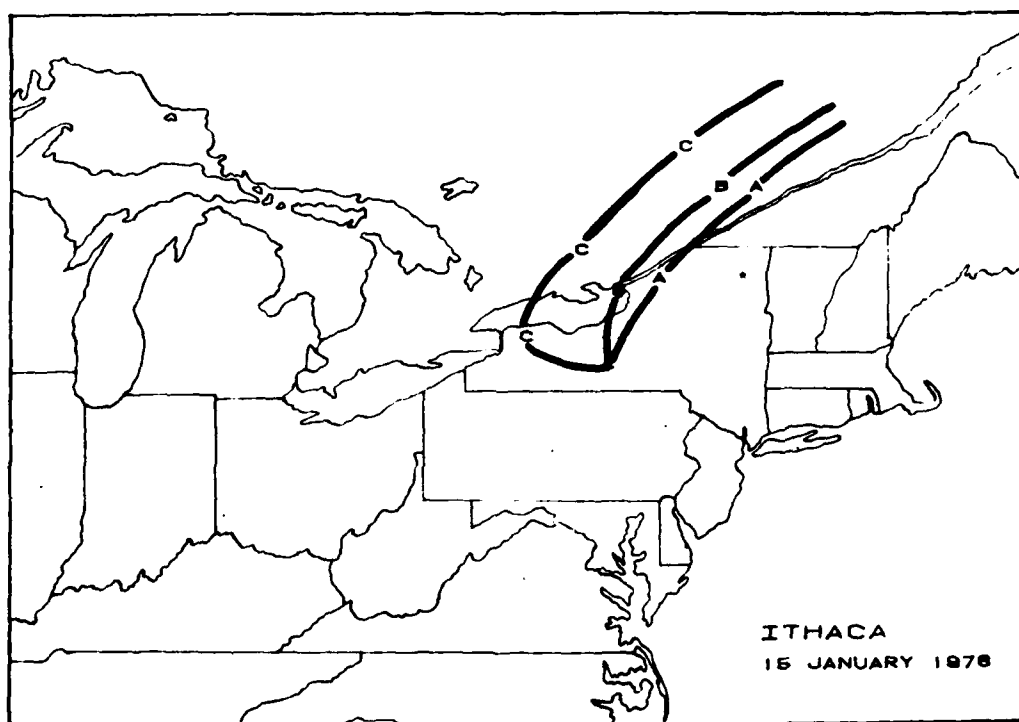
MAP3S Event - 11 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	37	13	15	2.2
Deposition (mg/m^2)	1.50	50	38	1.6

Sample volume - 1980 ml

$$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.96$$

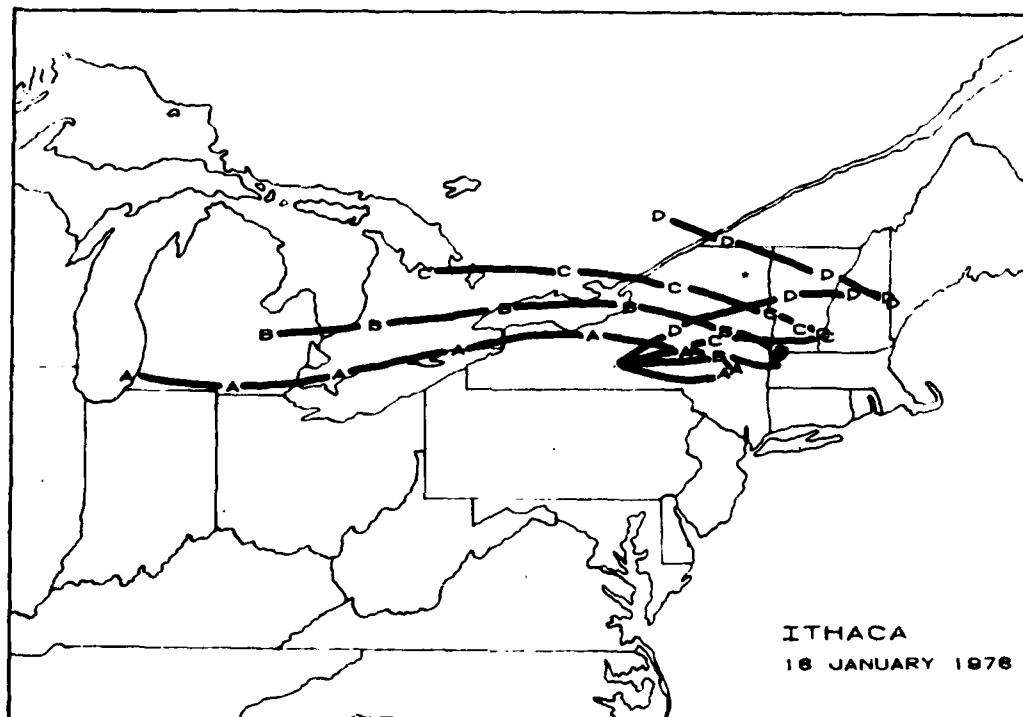
Figure 59. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 11 January, 1978.



MAP3S Event - 15 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	16	5.3	20	4.1
Deposition (mg/m^2)	0.41	9.2	22	-
Sample volume - 890 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.66$				

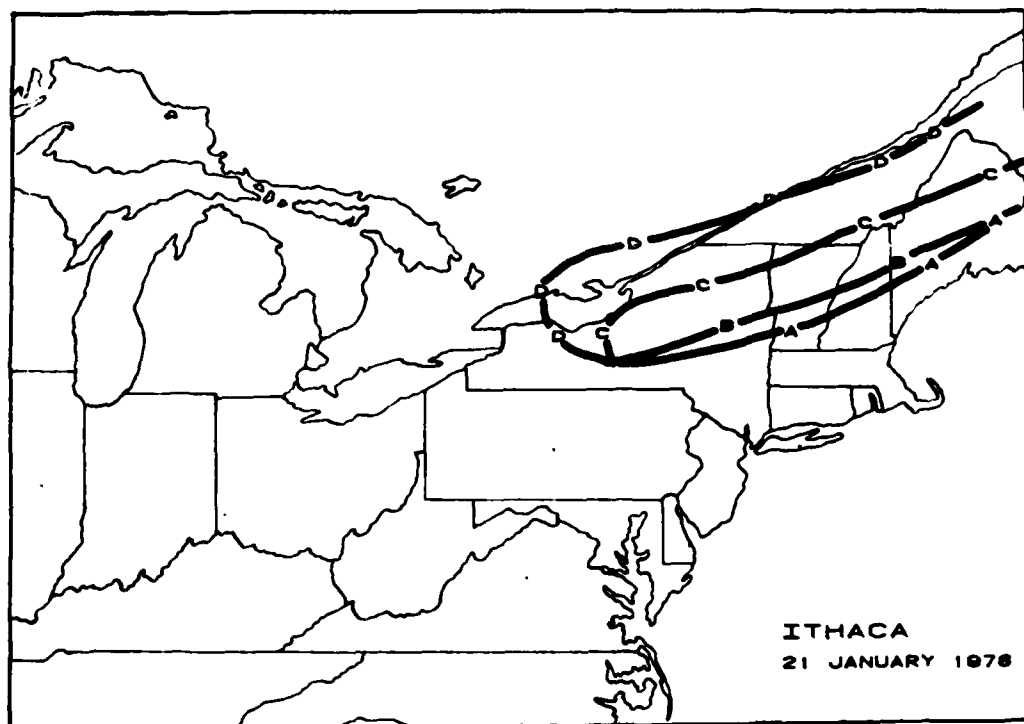
Figure 60. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 15 January, 1978.



MAP3S Event - 19 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	20	2.9	12	2.2
Deposition (mg/m^2)	0.54	7.9	21.1	0.3
Sample volume - 1390 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.25$				

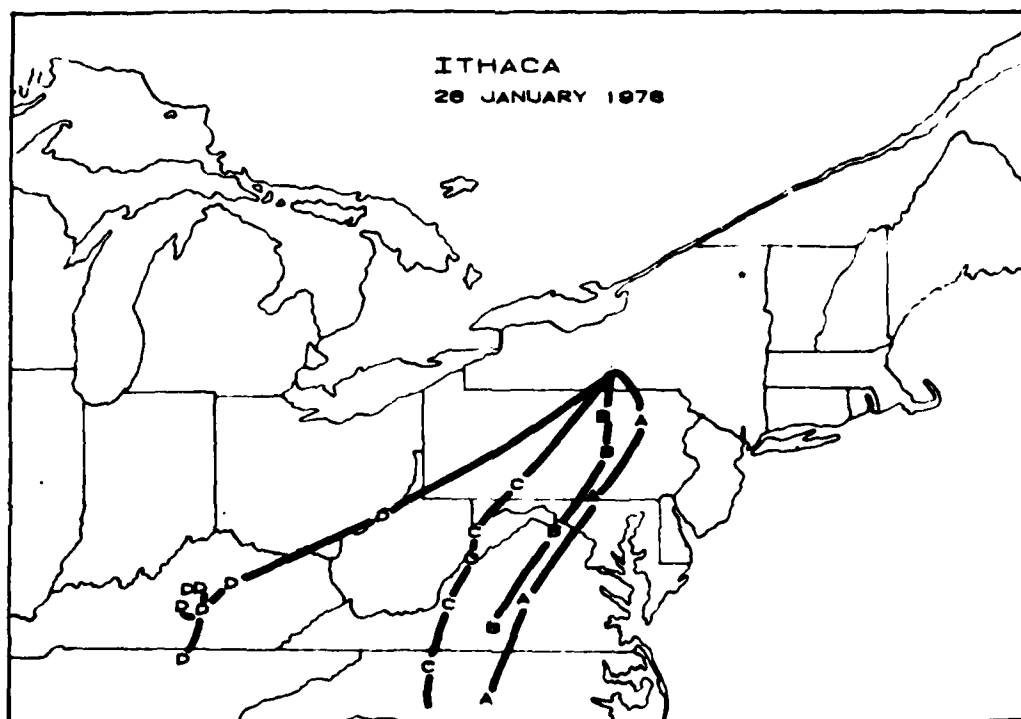
Figure 61. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 19 January, 1978.



MAP3S Event - 22 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	14	2.8	4.2	0.5
Deposition (mg/m^2)	0.17	4.2	4.1	-
Sample volume - 770 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 1.48$				

Figure 62. ARL-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 22 January, 1978.



MAP3S Event - 27 January 1978

	$[H^+]$	$[SO_4^{=}]$	$[NO_3^-]$	$[NH_4^+]$
Concentration ($\mu\text{mole/liter}$)	45	22	22	1.4
Deposition (mg/m^2)	0.51	23	15	0.3
Sample volume - 540 ml				
$[H^+]_L + [NH_4^+]/2[SO_4^{=}] + [NO_3^-] = 0.70$				

Figure 63. ARI-ATAD trajectories and MAP3S precipitation chemistry for the Ithaca event of 27 January, 1978.

as was the case for Whiteface Mountain. An ideal comparison can be made between "Canadian" air mass (January 22, Figure 62) and "Ohio Valley" air mass (January 27, Figure 63). The amount of total precipitation was about the same, so that no "dilution" bias exists:

	$\text{L}[\text{H}^+]$ ($\mu\text{mole/L}$)	$\text{SO}_4^{=}$ ($\mu\text{mole/L}$)	NO_3^- ($\mu\text{mole/L}$)
Canadian air Jan. 22 at ITH	14	2.8	4.2
Ohio Valley air Jan. 27 at ITH	45	22	22

Both events were initiated by developing cyclones moving southwest-to-northeast along the eastern United States. The system of 21 January developed into a coastal storm as it moved offshore, producing the largest snowfall of the year for many stations in the Northeast. Boston, Massachusetts recorded 21 inches of snowfall, while many stations in Connecticut received in excess of 15 inches. It should be noted that this air mass was not stagnant and was one of several cyclones that moved along the east coast during January.

In contrast, the precipitation which fell 25 and 26 January 1978 was primarily rain or mixed rain with snow and resulted from a rapidly developing, intense cyclone which passed over the Great Lakes. The central pressure of the system fell below 960 mb on 26 January as it passed New York State. The more northerly track of this latter system resulted in the warmer, southerly wind component illustrated in the ARL-ATAD analysis of Figure 63.

The event deposition values are as indicated in Figures 62 and 63, with the 27 January case contributing roughly four to five times that of the 22nd. However, individual case studies must not be taken

out of context and their relative contribution to total wet deposition must always be considered. When the case of 27 January is compared with wet deposition for the entire month, the following picture emerges:

	$\text{SO}_4^{=}$ (mg/m ²)	NO_3^{-} (mg/m ²)	$\text{L}[\text{H}^+]$ (mg/m ²)
All events except Ohio Valley	81.4 total or 16 per event	113.4 total or 23 per event	2.79 total or 0.6 per event
January 27-28 Ohio Valley	23.3 per event or 33% of total monthly wet deposition	15 per event or 8% of total monthly wet deposition	0.51 per event or 6% of total monthly wet deposition

Obviously, considerably more data are needed to arrive at a general conclusion, but the emerging picture seems to be such that much of the wintertime deposition in the northeastern part of the United States is due to air masses from the north northwest-to-northeast sector. This is in spite of the findings that the concentration of pollution-related ions in precipitation is very low. Different results might be found above 700m.

A final remark seems to be appropriate in regard to "wet deposition." As is seen in Figure 29a, the one-year average precipitation at Whiteface Mountain (solid line) is higher in winter (snow) by almost a factor or two than in summer (rain). Most of the winter snow is caused by air masses from the 270-90° sector. Even though this precipitation shows lower concentration than "summer" rain from the 180-270° sector, the amount of ions deposited is still appreciable. Furthermore, the impact of rain, if any, is almost immediate in the form of runoff. The impact of snow, if any, can be cumulative and delayed.

3.6 Impact of Hurricanes David and Frederic on Concentration and Deposition at MAP3S Stations

Two major hurricane events of September 1979 provide a unique opportunity to compare typical MAP3S measurements to those where intense washout processes had been at work. The marine origin of the hurricane, coupled with the diluting effect of massive amounts of rainfall, should make the ion concentrations in precipitation the lowest possible in pollutants, particularly $\text{SO}_4^{=}$, NO_3^- , and H^+ . Hurricane David, 6-7 September 1979, and Frederic, 14-15 September 1979, provide such a data set, since the effects of these two systems were felt throughout the northeastern United States.

Figure 64 shows the six-hour rainfall totals for September 1979 at Whiteface Mountain. The extreme amounts delivered by David over the two-day period provide such an ultimately clean environment.

Figures 65 and 66 show the trajectories produced by the ARL-ATAD model for the two events. Both analyses show a strong southerly component, followed by a marked shift to the north northwest. These figures are in good agreement with 850 mb analysis of Falconer and Kadlecsek (1980).

Table 16 provides an overview of the regional concentration and total wet deposition for these two major storm systems. The day indicated in column one of Table 16 is not necessarily the day when rainfall occurred, but rather the date of MAP3S collection. Values of pH, or free hydrogen ion concentration, from this table suggest a revision might be necessary in the classical definition of the "normal" pH of 5.6. To obtain this theoretical hydrogen ion

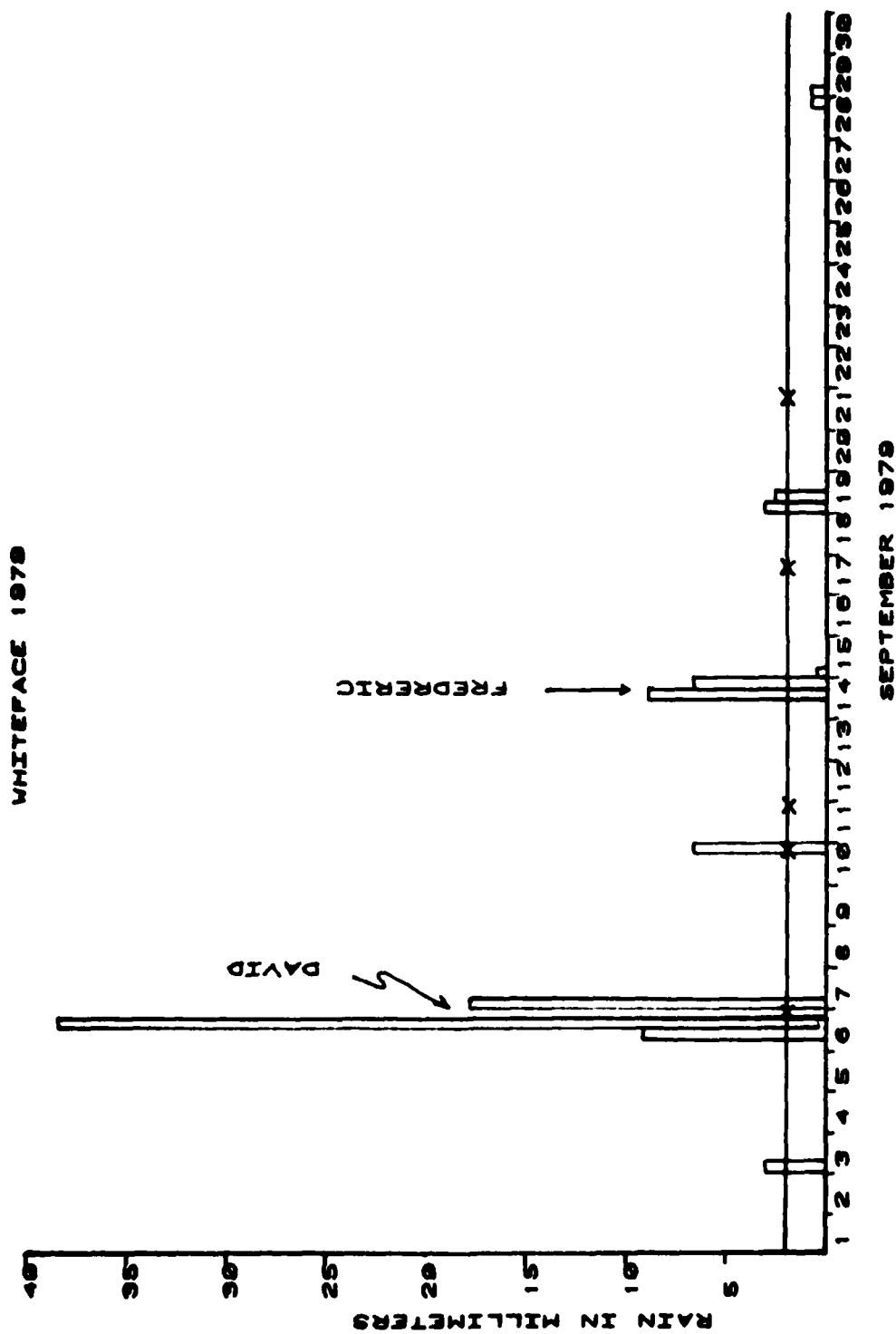


Figure 64. Six-hour rainfall totals recorded at Whiteface Mountain for Hurricanes David and Frederic, September 1979.

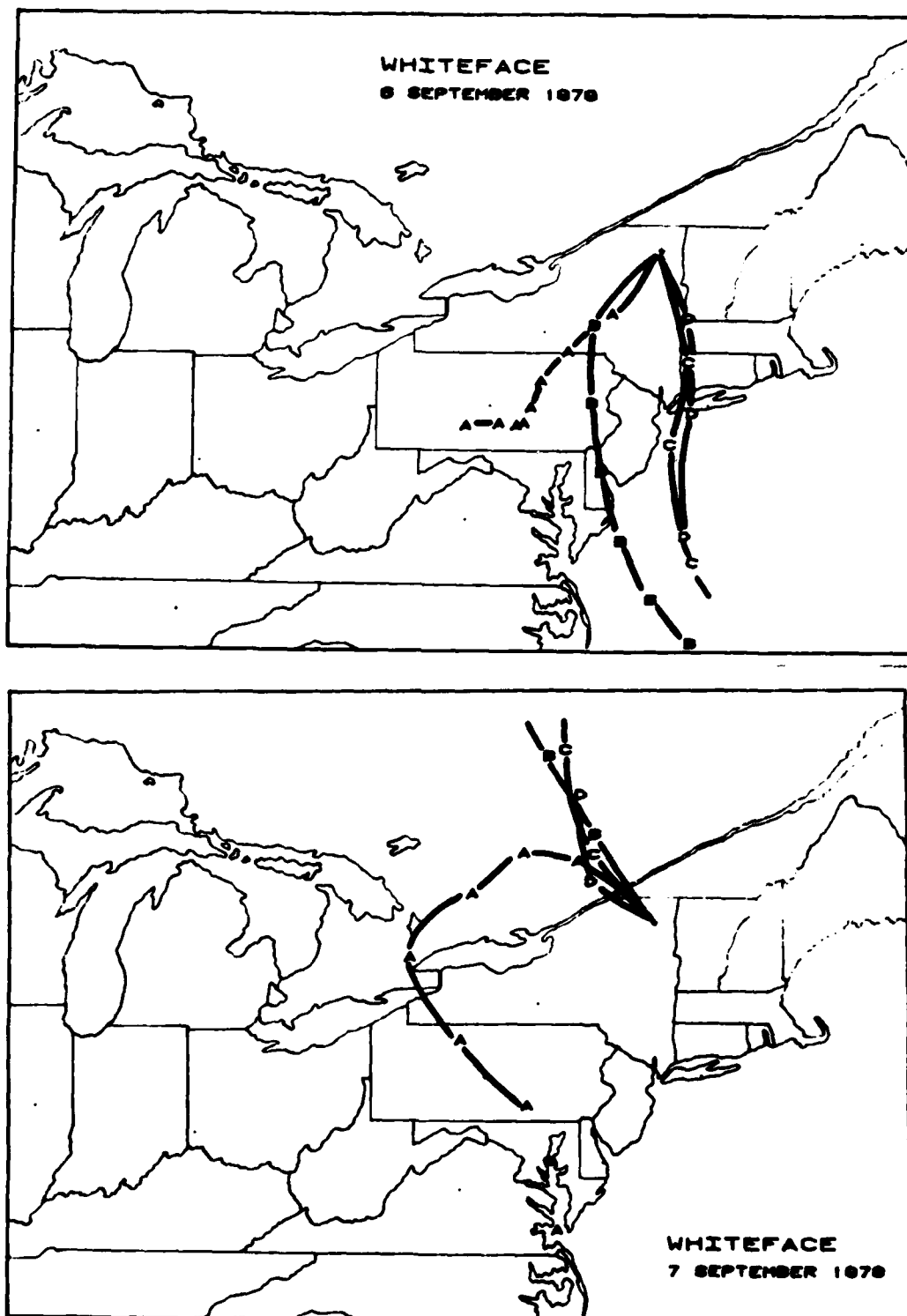


Figure 65. ARL-ATAD trajectories for Hurricane David, a) 6 September, and b) 7 September, 1979.

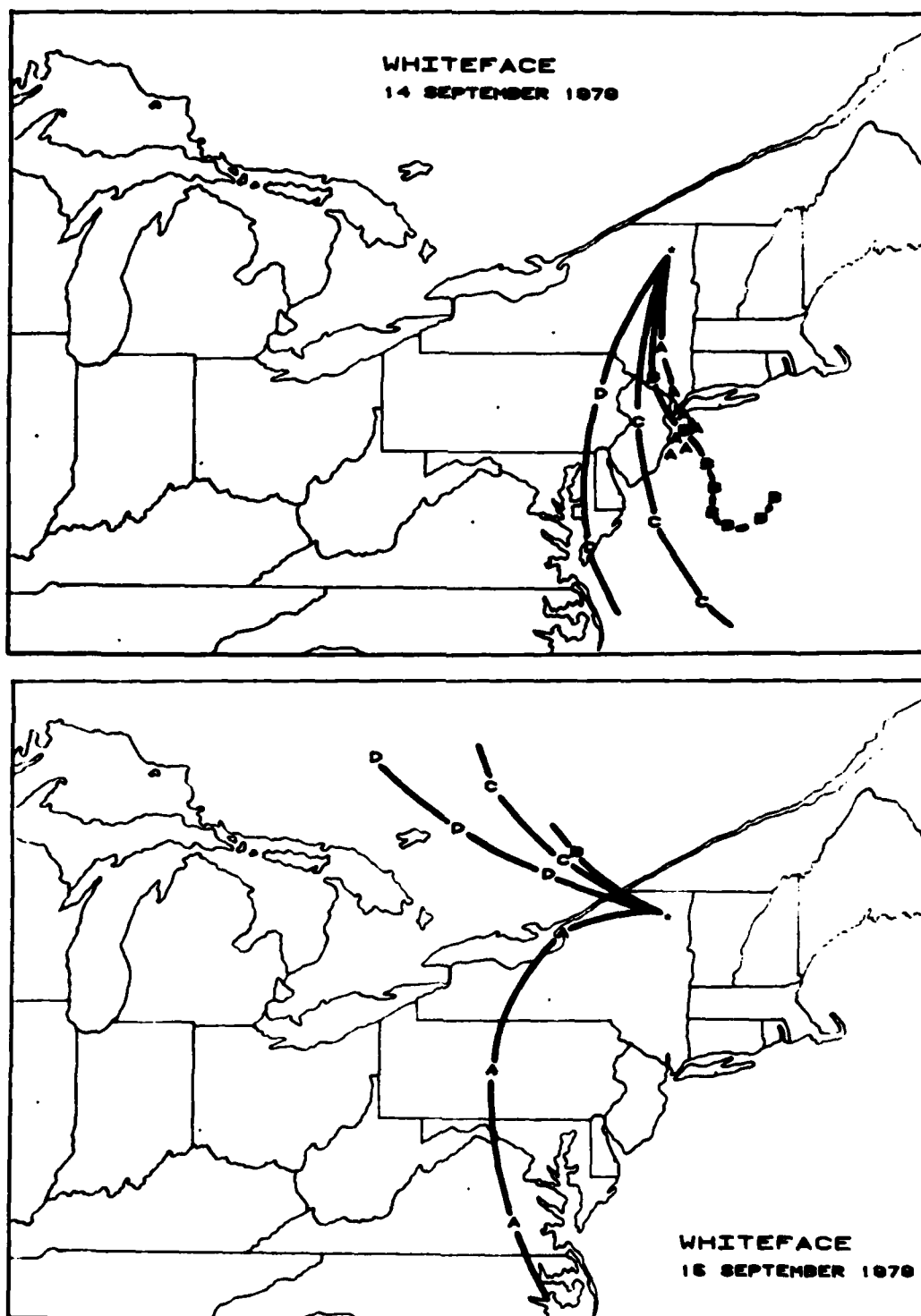


Figure 66. ARL-ATAD trajectories for Hurricane Frederic, a) 14 September, and b) 15 September, 1979.

concentration, it is assumed that only CO_2 contributes to the acidity of precipitation. Concentrations of approximately $2.5 \mu\text{mole/liter}$ are needed for the sample to have a pH of 5.6. However, no usable samples were obtained throughout the network that reached this hypothetical concentration.

The 7 September event for Ithaca most closely approximates this value with a concentration of $6 \mu\text{mole/liter}$ resulting in a pH of 5.2. Therefore, it is apparent that a pH of 5.6 may not be appropriate to describe a relevant and representative background hydrogen ion concentration in clean precipitation. The MAP3S measurements during an ultimately clean event of a hurricane tend to further substantiate the hypothesis that the natural pH of precipitation in the northeastern United States, and probably other places, cannot be explained on the basis of CO_2 alone.

With the exception of Brookhaven and Lewes, both coastal sites, the measurements of Table 16 suggest several important conclusions for the September 6 event. In particular, there exists a regional uniformity of very low concentration values throughout the MAP3S network for all major ions in precipitation, in particular for the pollution-related ions of H^+ , $\text{SO}_4^{=}$, and NO_3^- . The concentration and deposition of David at several MAP3S stations could be summarized as follows:

TABLE 16

PRECIPITATION CHEMISTRY OF HURRICANES DAVID AND FREDERIC - SEPTEMBER 1979

DAY	P.T. (HRS)	S.V. (ML)	F[H] (UM/L) μg/m ²	I[H] (UM/L) μg/m ²	COND. UMH/CM	[SO ₄] (UM/L) μg/m ²	[NH ₄] (UM/L) μg/m ²	[NO ₃] (UM/L) μg/m ²	[Cl] (UM/L) μg/m ²	[NA] (UM/L) μg/m ²	[K] (UM/L) μg/m ²	[CA] (UM/L) μg/m ²	[Mg] (UM/L) μg/m ²
BROOKHAVEN, NY													
6	9.1	444	38 0.34*	18 0.16*	81	39 33.92*	10 1.63*	15 8.43*	540 173.48*	450 93.73*	8.5 3.01*	16 5.81*	43 9.47*
15	1.5	73	2.9										
ITHACA, NY													
3	3	930	78 1.48*	79 1.49*	32	33 60.13*	16 5.48*	16 18.82*	3.6 2.42*	.86 0.38*	.64 10.47*	1.2 0.91*	
7	20	3160	6 0.587*	8.5 0.58*	4	3.7 22.91*	2.2 2.56*	2.5 9.97*	.13 10.29*	1.2 1.74*	1.2 3.03*	.67 2.12*	
15	4	1080	26	45	14	15 31.74*	6.3 2.5*	11 15.03*	2.3 1.80*	1.6 0.81*	.77 0.66*	1.5 1.33*	.49 0.26*
LEWES, DE													
4	.3	6											
6	16	2083	8.1 0.544*	10 0.425*	23	13 55.05*	2.6 1.99*	4.1 10.81*	150 226.1*	110 107.5*	2.5 4.16*	5.4 9.20*	15 15.5*
15	1	482	13 0.126*	11 0.106*	8	8 7.55*	6.3 1.12*	5.1 3.11*	12 4.18*	12 2.71*	1.1 0.42*	.87 0.34*	2.1 0.5*
PENN STATE, PA													
3	5	2166	49 2.55*	48 2.50*	23	28 118.82*	17 15.56*	14 38.37*	3.9 6.11*	1.1 1.12*	.98 1.69*	1.6 2.83*	
6	12.7	2141	11 0.45*	15 0.56*	6	5.4 22.65*	1.3 1.02*	4.4 11.92*	2.4 3.72*	9.4 9.44*	7 11.96*	.95 1.66*	
7	1	37		229 0.15*	130	150 10.87*	100 1.36*	190 8.90*	25 0.67*	11 0.19*	9.1 0.27*	50 1.51*	16 0.29*
15	4.3	448	31 0.26*	32 0.29*	16	14 12.29*	7.4 1.22*	11 5.24*	4.1 1.33*	4.1 0.86*	1.9 0.68*	1.6 0.59*	.62 0.14*
VIRGINIA													
4	7	2000	76 3.1*	100 4.06*	40	34 133.22*	13 9.57*	22 55.68*	8.9 12.88*	2.2 2.06*	1.4 2.23*	.77 1.26*	
7	2.5	4800	8.1 0.97*	13 1.27*	6	4.4 41.4*	2.3 4.06*	3.6 21.87*	4.4 15.28*	4.4 9.91*	.37 1.42*	.9 3.53*	.53 1.26*
8	.5	72	126 0.18*	135 0.19*	69	100 14.11*	67 1.78*	45 4.10*	12 0.63*	10 0.34*	9.3 0.53*	15 0.88*	4.1 0.15*
15	17	709		40 0.58*	21	22 30.56*	15 3.92*	13 11.66*	21 10.77*	19 6.32*	1.2 0.68*	1.8 1.04*	2.2 0.77*
WHITEFACE MT., NY													
6		3595	22 1.61*	14 1.03*	8	8.1 57.05*	5.2 6.88*	6.1 27.75*	6.2 16.13*	3.9 3.20*	3.3 3.73*	2.5 2.35*	9.2 9.25*
10		1419	15 0.43*	45 1.3*	19	25 69.5*	12 6.27*	5.5 9.88*	16 16.43*	0.7 0.47*	0.7 0.79*	0.5 0.71*	d.l.
17		1151	21 0.49*	15 0.35*	6	5.4 12.17*	0.85 0.36*	4.7 6.85*	3.2 2.66*	0.82 0.44*	d.l.	0.5 0.47*	d.l.

Concentration (in $\mu\text{mole/L}$) and Deposition (in mg/m^2) for Hurricane David (the deposition values are listed in parenthesis)

	$[\text{SO}_4^{=}]$	$[\text{NO}_3^{-}]$	$\text{L}[\text{H}^{+}]$	$[\text{Na}^{+}]$
WFM	8 (57)	6 (28)	14 (1)	2
ITH	4 (23)	3 (10)	9 (0.6)	1
PEN	5 (23)	4 (12)	15 (0.7)	1
VIR	4 (41)	4 (22)	13 (1.3)	3
LEW	13 (53)	4 (11)	10 (0.4)	110
BRO	39 (34)	15 (8)	18 (0.2)	450

The two coastal sites BRO and LEW show higher concentration values for sulfates commensurate with very high concentration values for sodium and all other marine-related ions.

The following order can be established in regard to the concentration values for David in comparison with other values observed during the entire year of 1979 for the stated ions.

	$[\text{SO}_4^{=}]$	$[\text{NO}_3^{-}]$	$\text{F}[\text{H}^{+}]$	$[\text{Na}^{+}]$
WFM	6th lowest	2nd lowest	2nd lowest	low
ITH	2nd lowest	2nd lowest	lowest	low
PEN	2nd lowest	3rd lowest	lowest	low
VIR	lowest	2nd lowest	lowest	low
LEW	14 out of 49	2nd lowest	lowest	very high
BRO	30 out of 41	16 out of 41	12 out of 67	highest value for 1979

The deposition values resulting from Hurricane David are slightly below or slightly above the respective mean deposition values for the entire year, while the concentration ($\mu\text{mole/L}$) of pollution-related material ($\text{SO}_4^{=}$, NO_3^{-} , H^{+}) was one of the lowest in precipitation recorded for the entire year 1979. The resulting deposition (mg/m^2) can be classified as producing about average values:

	$\frac{(\text{SO}_4^{=})_{\text{David}}}{(\text{SO}_4^{=})_{\text{Mean}}}$	$\frac{(\text{NO}_3^{-})_{\text{David}}}{(\text{NO}_3^{-})_{\text{Mean}}}$	$\frac{\text{L}[\text{H}^{+}]_{\text{David}}}{\text{L}[\text{H}^{+}]_{\text{Mean}}}$
WFM	57/42	28/25	1/1.0
ITH	23/42	10/23	0.6/1.1
PEN	23/42	12/26	0.7/1.0
VIR	41/36	22/20	1.3/1.0

The impact of Hurricane Frederic on the precipitation chemistry of the MAP3S stations was mixed. There is no uniform pattern, partly because of the different storm trajectory from September 14 to September 15.

The ranking of concentration values for Hurricane Frederic is presented below:

	$[\text{SO}_4^{=}]$	$[\text{NO}_3^{-}]$	$\text{L}[\text{H}^{+}]$
WFM	2nd lowest	lowest	3rd lowest
ITH	9 out of 53	4th lowest	4th lowest
PEN	11 out of 66	3rd lowest	7th lowest
VIR	22 out of 52	13 out of 52	9 out of 50
LEW	4th lowest	4th lowest	4th lowest

Concentration (in [$\mu\text{mole/L}$]) and Deposition (in [mg/m^2])
for Hurricane Frederic (the deposition values are listed
in parenthesis)

	$[\text{SO}_4^{=}]$	$[\text{NO}_3^{-}]$	$\text{L}[\text{H}^{+}]$	$[\text{Na}^{+}]$
WFM	5(12)	5(7)	15(0.4)	1
Mean deposition for 79	(42)	(25)	(1.0)	
ITH	15(31)	11(15)	45(1.0)	1
Mean deposition for 79	(42)	(23)	(1.1)	
PEN	14(13)	11(6)	32(0.3)	4
Mean deposition for 79	(42)	(26)	(1.0)	
VIR	22(31)	13(12)	40(0.6)	19
Mean deposition for 79	(36)	(20)	(1.0)	
LEW	8(8)	5(3)	11(0.1)	12
BRO	N.D.	H.D.	N.D.	N.D.

The deposition of pollutant-related material ($\text{SO}_4^{=}$, NO_3^{-} , H^{+})
resulting from Frederic was below average for all MAP3S stations
that reported a precipitation event.

Therefore, the concentrations measured during these events
which might be classified as nature's ultimate cleansing mechanism,
can be used as a benchmark to define a "background" level for "acid
rain."

4.0 SPATIAL VARIABILITY IN WET DEPOSITION FOR THE EASTERN UNITED STATES

4.1 Analysis Procedure

While several North American precipitation chemistry monitoring networks operate independently, it is nevertheless possible to correlate their results through proper analysis techniques (Pack, 1980). Two programs offering regional coverage, accessible data, and reliable quality control are the Multistate Atmospheric Power Production Pollution Study (MAP3S) and the National Atmospheric Deposition Program (NADP). Even though MAP3S is event-oriented while NADP collects weekly samples, their integrated ion deposition measurements are compatible when compared over time scales in excess of one year. Figure 67 and Table 17 show the location of the MAP3S and NADP sites of the eastern United States which collected data for the majority of 1979. All eight MAP3S stations were included, but several NADP sites were excluded due to insufficient data.

Total wet deposition was normalized per centimeter of precipitation to allow for an inter-site comparison of the four dominant ions in precipitation. To insure complete objectivity, spatial distributions of normalized wet deposition were analyzed using Synagraphic Mapping System (SYMAP), developed by the Laboratory for Computer Graphics and Spatial Analysis, Harvard University (Dougenik and Sheehan, 1975).

The normalized wet deposition values were compared with standard rain gauge measurements to obtain estimates of the actual total wet deposition of the four dominant ions. National Climatic Center

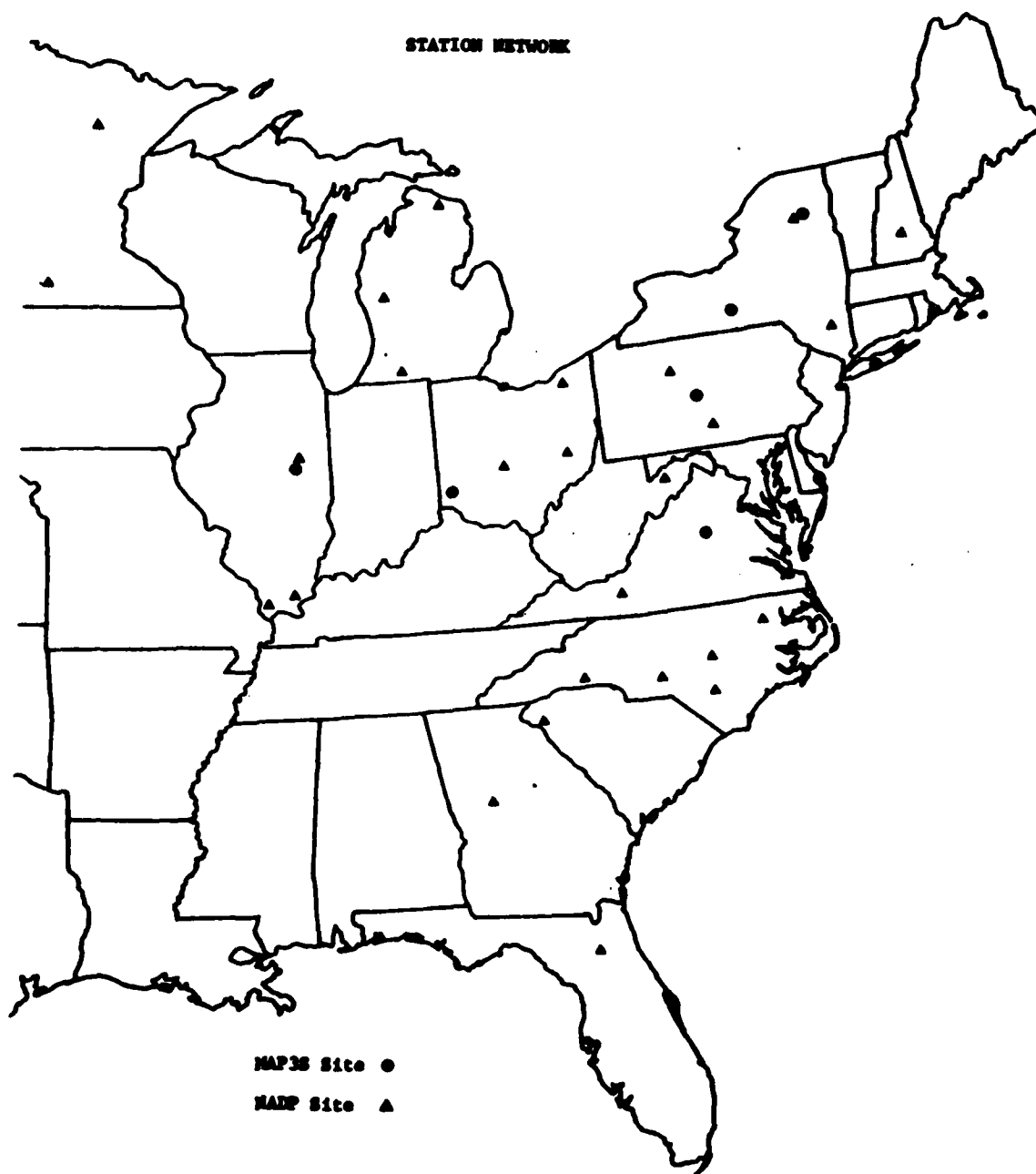


Figure 67. MAP3S and NADP station network used for 1979 spatial deposition analysis.

TABLE 17

NADP Stations Used in 1979 Inter-Comparison Study

<u>State</u>	<u>Site Name</u>	<u>Latitude</u>	<u>Longitude</u>
Florida	Bradford Forest	29.97	82.20
Georgia	Georgia Station	33.18	84.40
Illinois	Bondville	40.05	88.37
Illinois	SIU	37.70	89.27
Illinois	Dixon Springs Ag. Ctr.	37.43	88.67
Michigan	U. Mich. Biological Sta.	45.57	84.68
Michigan	Kellogg Biological Sta.	42.48	85.38
Michigan	Wellston	44.22	85.85
Minnesota	Marcell Exp. Forest	47.50	93.47
Minnesota	Lamberton	44.25	95.32
Nebraska	Mead	41.09	96.50
New Hampshire	Hubbard Brook	43.95	71.70
New York	Huntington Wildlife	44.00	74.22
New York	Stilwell Lake-West Point	41.35	74.03
North Carolina	Lewiston	36.13	77.17
North Carolina	Coweeta	35.02	83.45
North Carolina	Piedmont Research Sta.	35.67	80.57
North Carolina	Clinton Crops Res. Sta.	35.01	78.28
North Carolina	Finley	35.73	78.68
North Carolina	Research Triangle Park	35.87	78.78
Ohio	Delaware	40.28	83.06
Ohio	Caldwell	39.78	81.52
Ohio	Wooster	40.77	81.93
Pennsylvania	Kane Exp. Forest	41.55	78.77
Pennsylvania	Leading Ridge	40.55	77.93
South Carolina	Clemson	34.67	82.83
Virginia	Horton's Station	37.18	80.42
West Virginia	Parsons	39.10	79.65

rainfall data were considered to be an independent reliable source of total precipitation. Since the normalized deposition values integrated over the entire year contain no seasonal bias, this technique was considered acceptable in terms of producing estimates of annual total wet deposition.

4.2 Gridded Emission Inventory

To evaluate adequately the chemical quality of precipitation and investigate possible source-receptor relationships, a detailed emission inventory is needed. The MAP3S emission inventory was used here to sum selected emissions per square latitude and longitude for the eastern United States. The MAP3S emission inventory was compiled of data extracted from the National Emissions Data System and the Federal Power Commission. It was updated using corrections provided by MAP3S and by the Sulfate Regional Experiment. The five (5) pollutants routinely measured were:

- total particulates
- sulfur dioxide
- nitrogen oxides
- hydrocarbons
- carbon monoxide.

Pollutant emissions were grouped into classifications of point or area sources. Point sources were defined as stationary sources with the potential of emitting at least 100 tons per day of any of the five (5) criteria pollutants (Clark, 1980). Area sources were reported by county and included vehicular emissions, as well as industrial and residential heating. The geographical center of each county was used to locate the emissions in a particular grid.

The annual point source emissions per square latitude and longitude are depicted in Figure 68. Since over 90% of the total sulfur dioxide are from point sources, this summation of stationary sources is representative of the actual annual total. Nearly 57% of the total point source emissions of sulfur dioxide could be linked to bituminous coal-fired electric generating plants, 12% to primary metals industry, 7% to burning of bituminous coal for industrial fuel, and 4% to petroleum industrial sources (Clark, 1980). The contribution of the point sources having stack heights greater than 100 meters is shown in Figure 69.

The total nitrogen oxide emissions of Figure 70 are closely correlated with large population density centers. Total point source emissions and area source contributions were found to be of the same order of magnitude. Two-thirds of the point source emissions are from the burning of fuels at electric generating plants, while over 80% of area sources are the result of vehicular exhaust.

4.3 Measured and Estimated Regional Wet Deposition Distributions

Figures 71 through 74 show the normalized wet deposition per centimeter of precipitation for 1979 for $\text{SO}_4^{=}$, NO_3^- , H^+ , and NH_4^+ , respectively. These objective analyses, using the procedure described earlier in Chapter 4.1, present a rather uniform east-west pattern for $\text{SO}_4^{=}$ and NO_3^- . A slightly more complex picture emerges for H^+ and NH_4^+ .

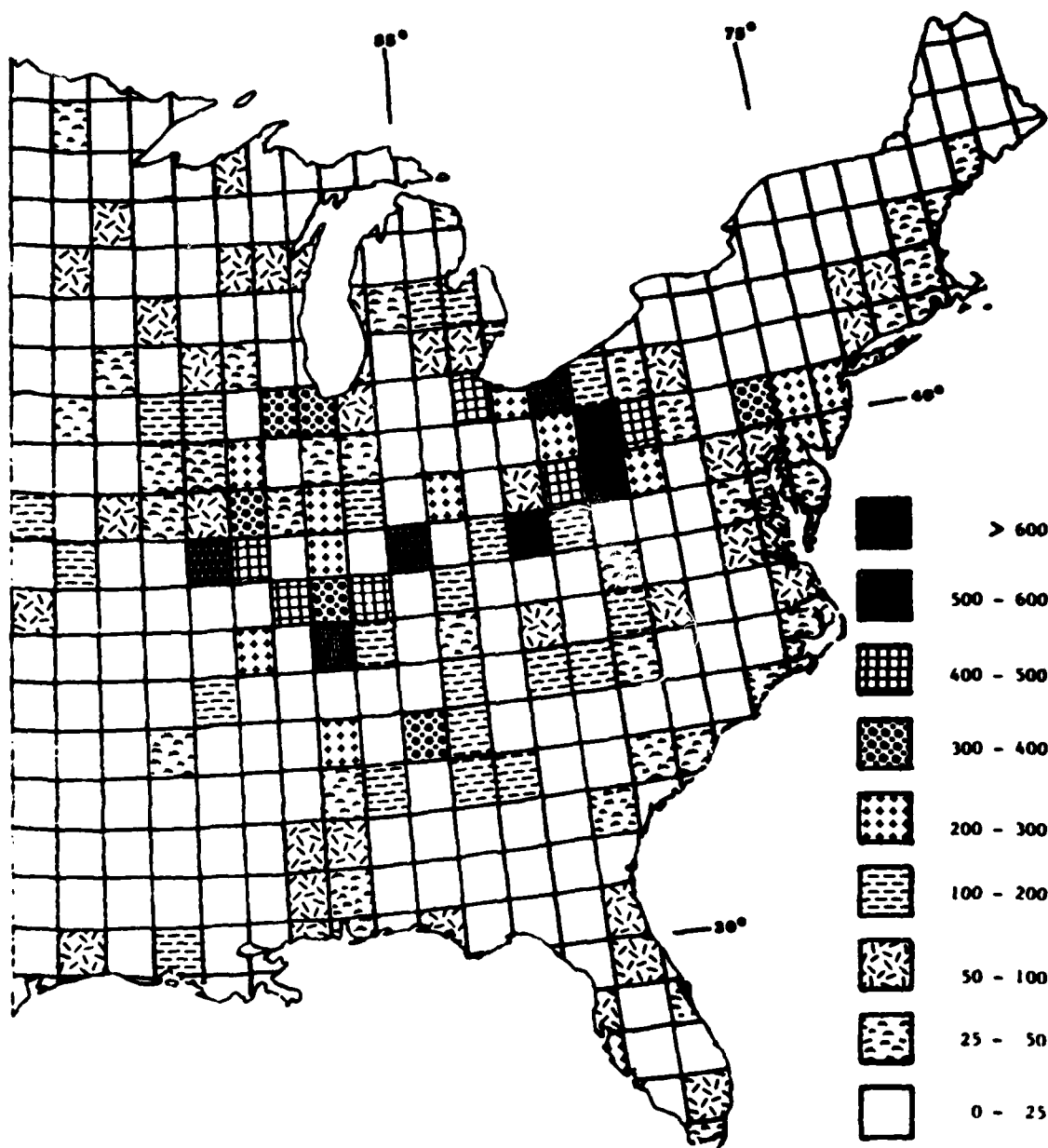


Figure 68. Gridded annual point source SO_x emissions (10^6 kg/yr) for the eastern United States.

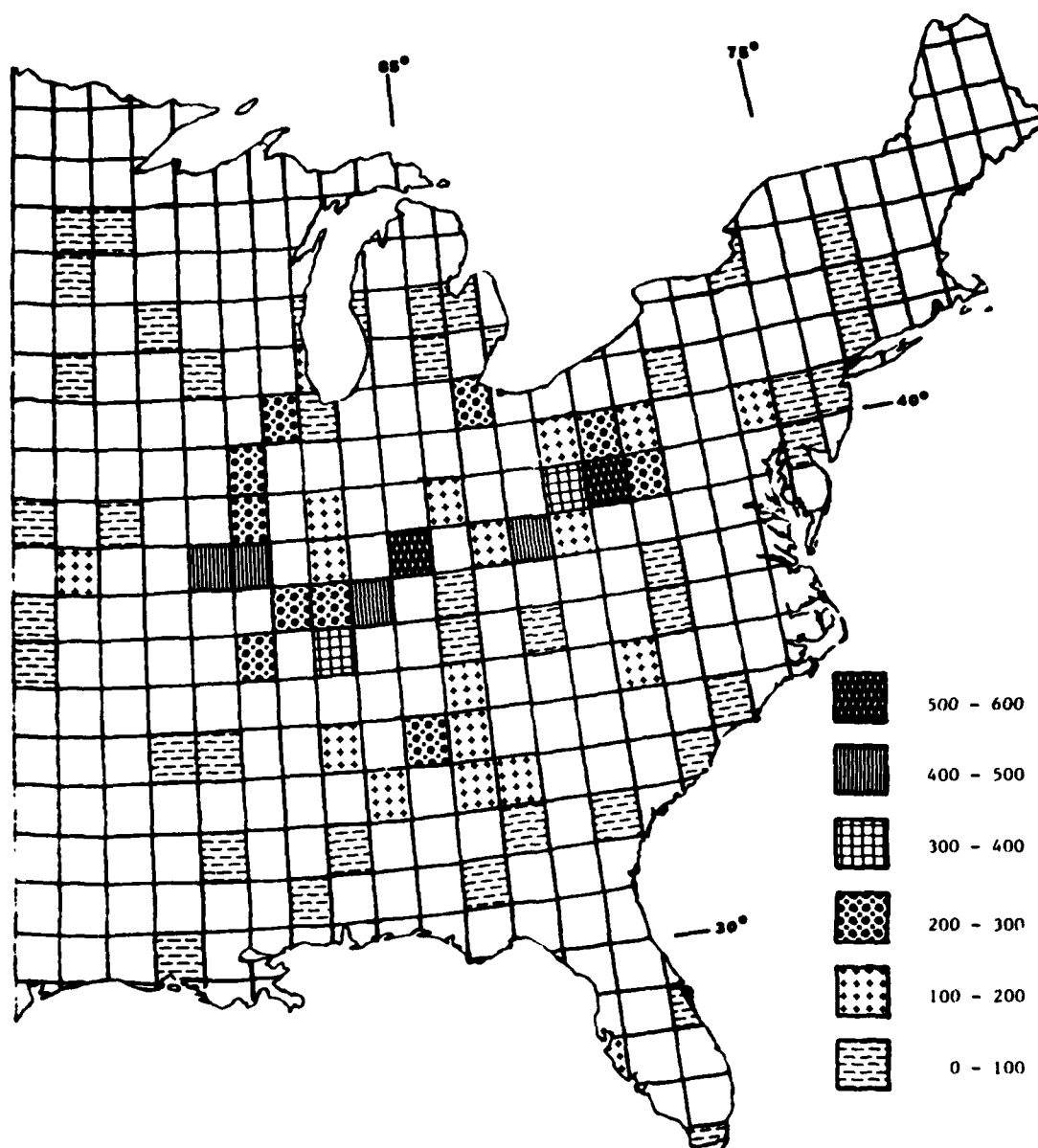


Figure 69. Gridded annual SO_x emissions (10^6 kg/yr) for point sources with stack height $> 100\text{m}$.

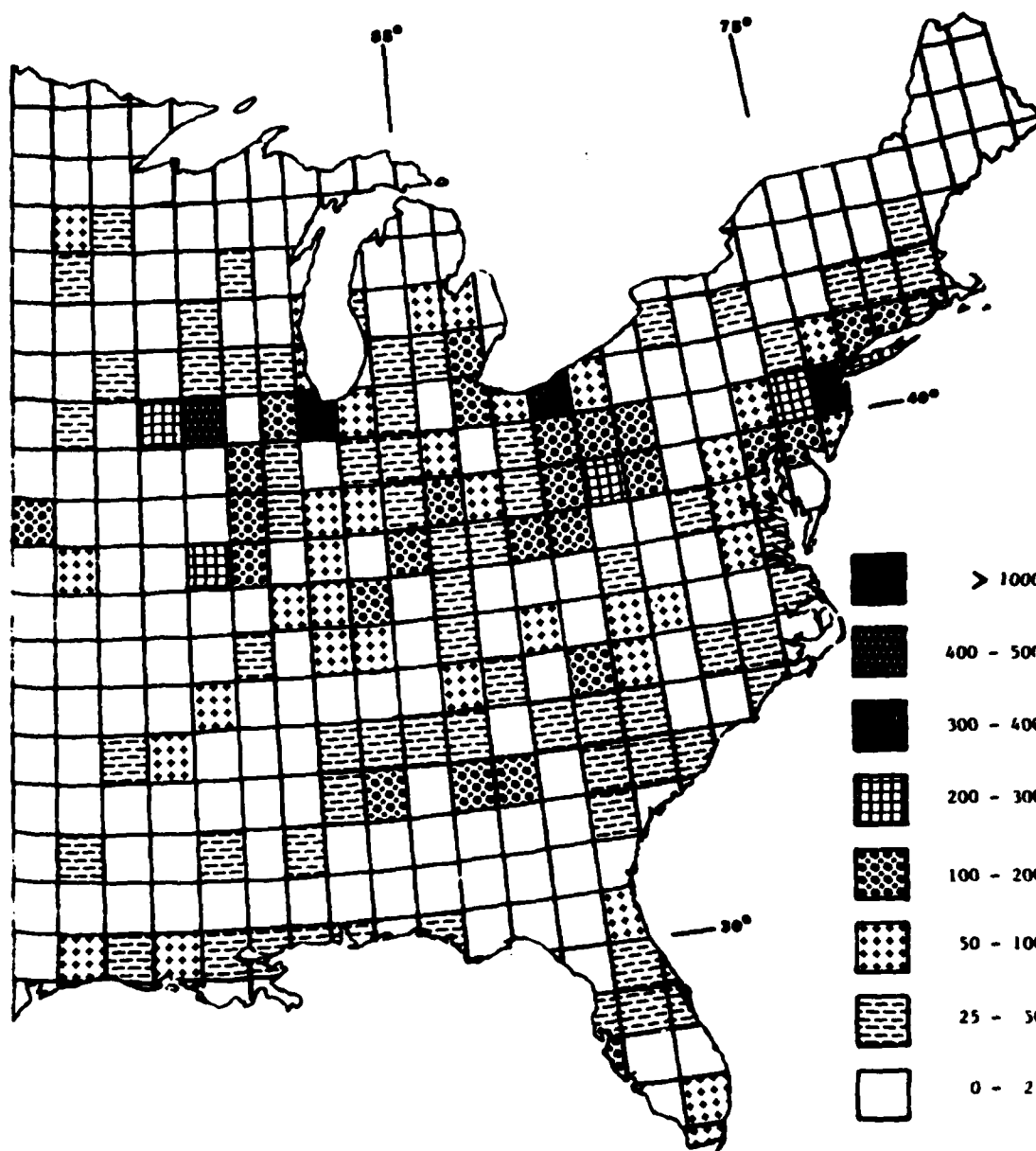


Figure 70. Gridded total annual NO_x emissions (10^6 kg/yr).

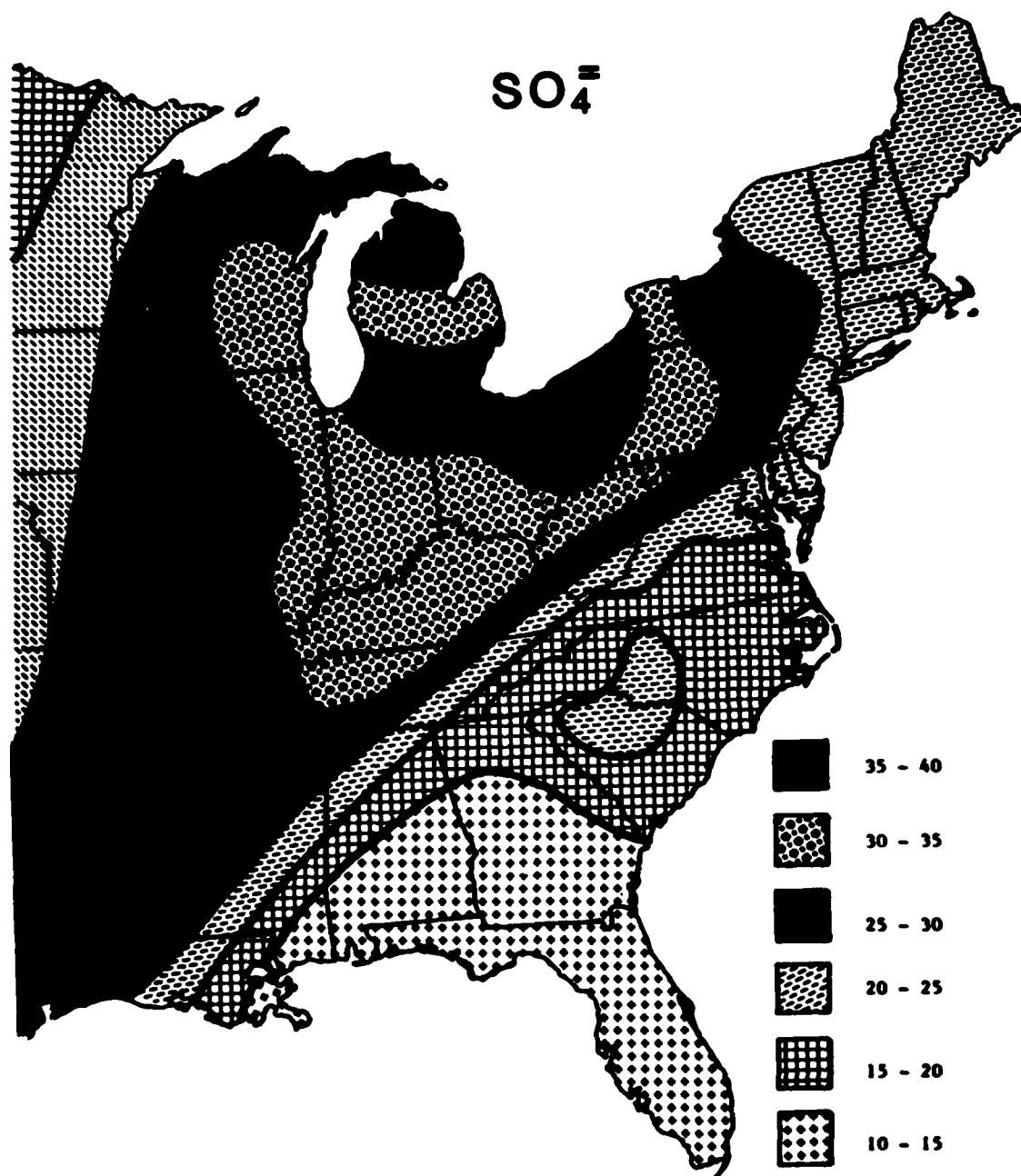


Figure 71. $\text{SO}_4^{=}$ deposition (mg/m^2) normalized per cm of precipitation for 1979.

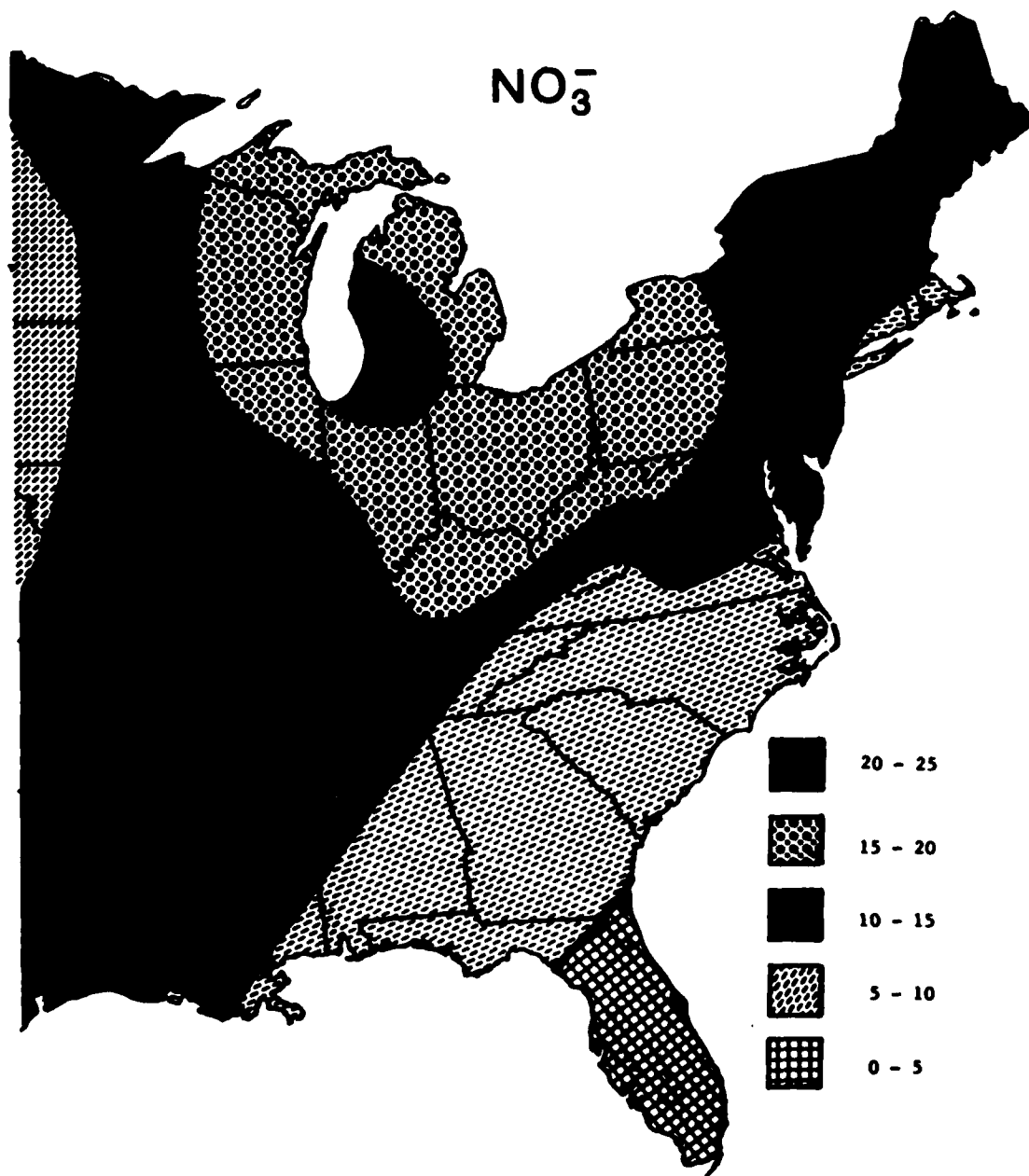


Figure 72. NO_3^- deposition (mg/m^2) normalized per cm of precipitation for 1979.

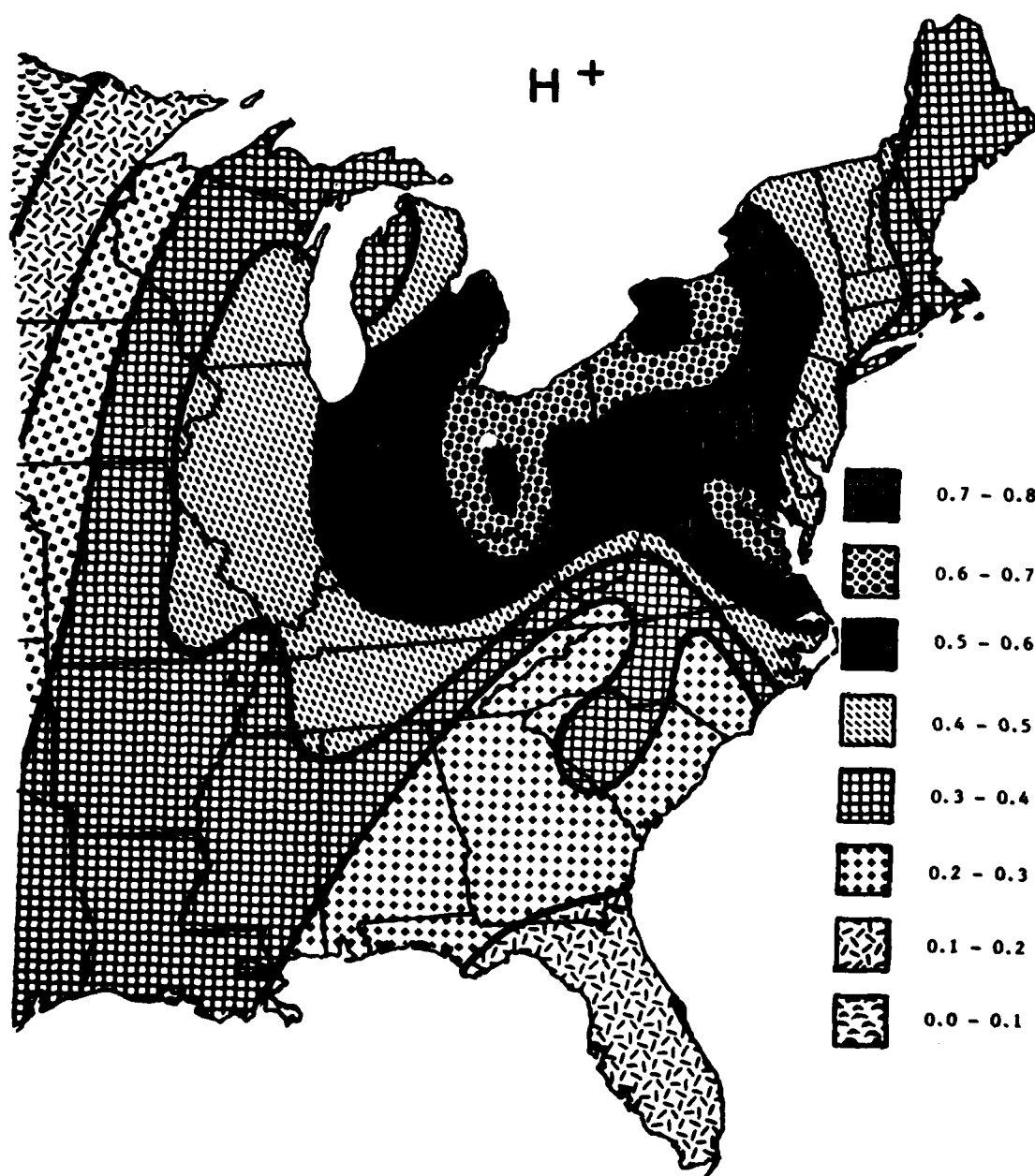


Figure 73. H^+ deposition (mg/m^2) normalized per cm of precipitation for 1979.

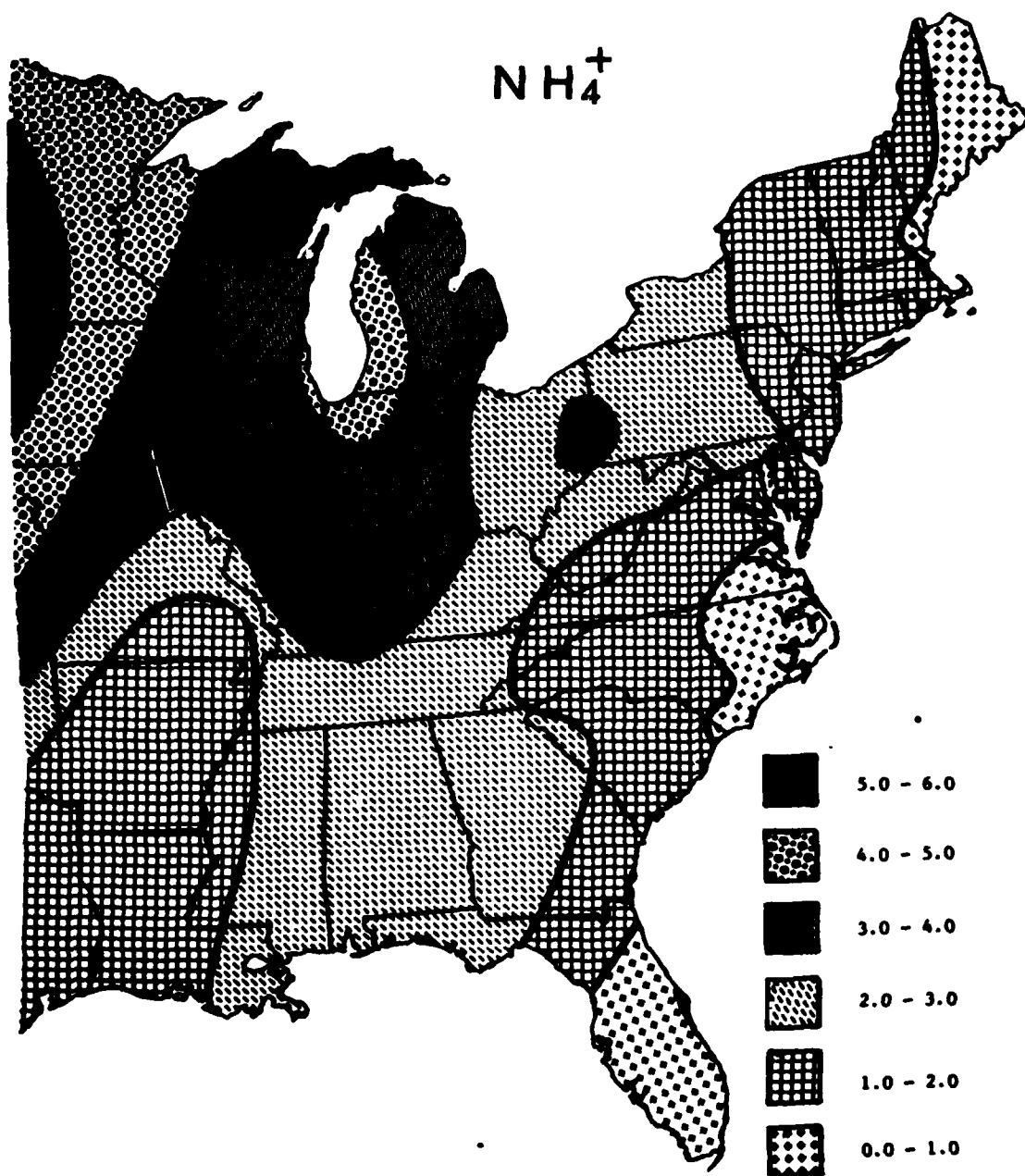


Figure 74. NH_4^+ deposition (mg/m^2) normalized per cm of precipitation for 1979.

The normalized $\text{SO}_4^{=}$ maximum of Figure 71 appears to correlate with the total point source emission patterns of sulfur dioxide, Figure 68. The secondary maxima in the Carolina's may be a result of the industrialized regions of the Southeast. Similar distribution characteristics are found in the normalized NO_3^- , Figure 72, when compared to the total nitrogen oxide emission of Figure 70. However, no direct source-receptor relationships are discernible from the data as a result of transport of pollutants over great distances.

The integrated normalized wet deposition of $\text{SO}_4^{=}$ and NO_3^- for 1979 shows a rather uniform gradient in almost every direction from the major emission area. No strong west-to-east gradient is found. Furthermore, no maximum located in the extreme northeastern United States is seen in these deposition values that would be indicative of increased wet deposition downwind of major emission areas. However, the effect of the Appalachian Mountains seems to be readily apparent as evidenced by the strong wet deposition gradients shown in Figures 71 and 72. The mountainous regions of the eastern United States above 2000 feet act to channel or divert low-level pollutants so as to shield the Virginia-Carolina area or act to produce different types of precipitation in each region.

Since the free hydrogen ion (H^+) deposition results from the contribution of various constituents including sulfuric acid, nitric acid and soil related components, such as Ca^{++} , Mg^{++} , and NH_4^+ , the spatial distribution of normalized H^+ deposition can be expected to be more complicated than either $\text{SO}_4^{=}$ or NO_3^- alone. This is verified in Figure 73. Localized maxima in H^+ wet deposition are evident and a strong gradient emerges to the west of 85° longitude. One can

speculate that soil-related material scavenged by precipitation might be responsible for the apparent change in free hydrogen ion deposition. Topography effects and the Carolina maximum are again evident. This is not surprising since a strong correlation exists between $\text{SO}_4^{=}$ and H^+ for the northeastern part of the United States (see Chapter 2).

The NH_4^+ distribution, Figure 74, is largely a function of natural sources and consequently displays no discernible source-receptor relationships. Increased NH_4^+ ion deposition to the west of 85° longitude correlates well with the decrease in free hydrogen ion deposition over the same geographic area (see Figure 73).

While these normalized deposition, or weighted concentration, values provide an indicator of precipitation quality per unit amount of precipitation, localized total deposition maxima may result due to enhanced precipitation events. Figures 75 through 78 depict estimates of total wet deposition derived from normalized deposition measured at a particular MAP3S or NADP site and measured local rainfall as discussed in Chapter 4.1. These computer-analyzed estimates reflect the localized nature of total rainfall over a time-span of a year. A precipitation maximum in Pennsylvania-West Virginia in excess of 186 cm is responsible for the increased deposition of all ions experienced in that region.

With the exception of localized maxima, the spatial analysis of estimated deposition exhibits essentially the same basic pattern as normalized deposition for $\text{SO}_4^{=}$, H^+ , and NH_4^+ . The estimated NO_3^- deposition pattern, Figure 76, was found to be more complex with

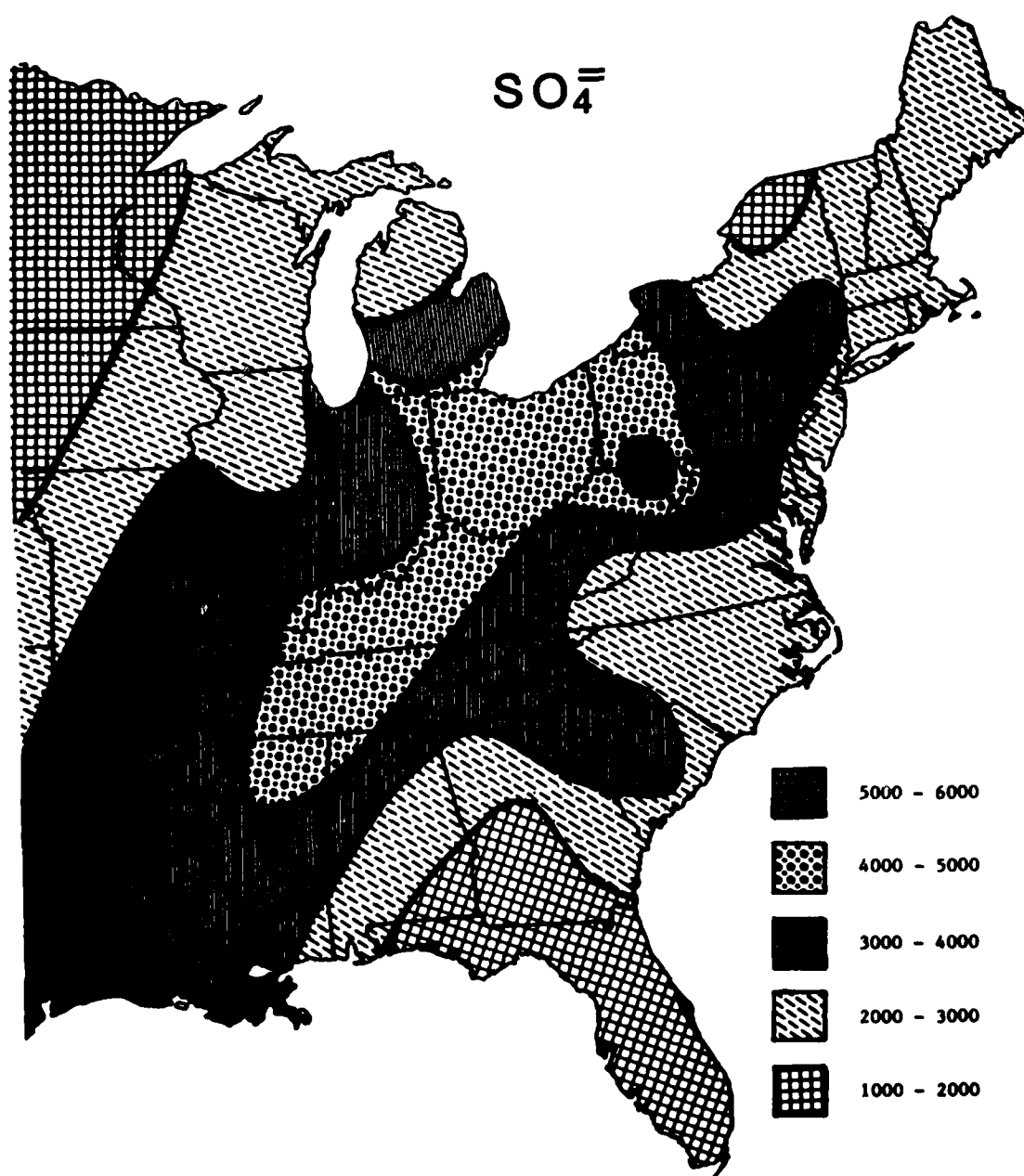


Figure 75. Estimated total $\text{SO}_4^{=}$ deposition (mg/m^2) for 1979.

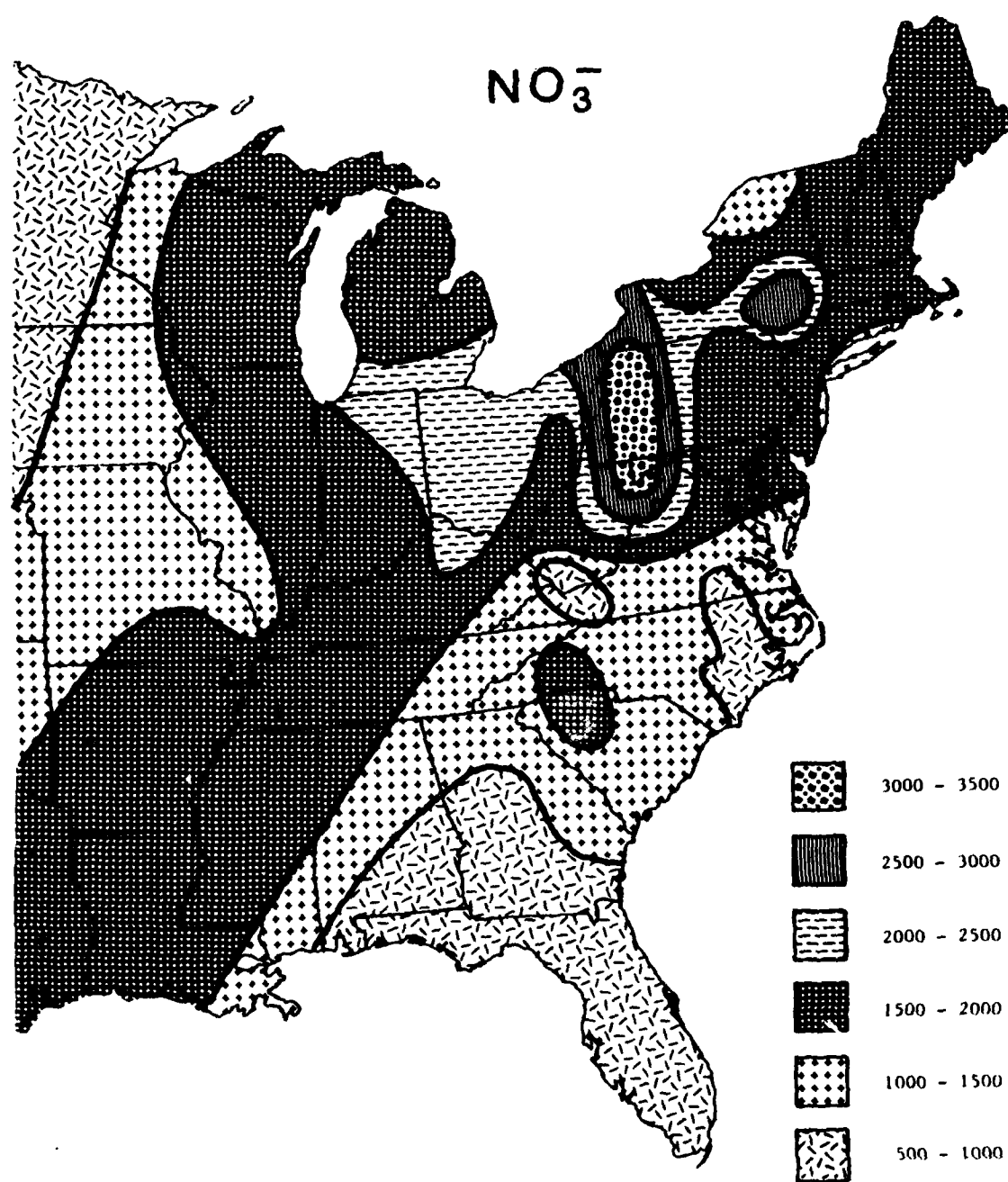


Figure 76. Estimated total NO_3^- deposition (mg/m^2) for 1979.

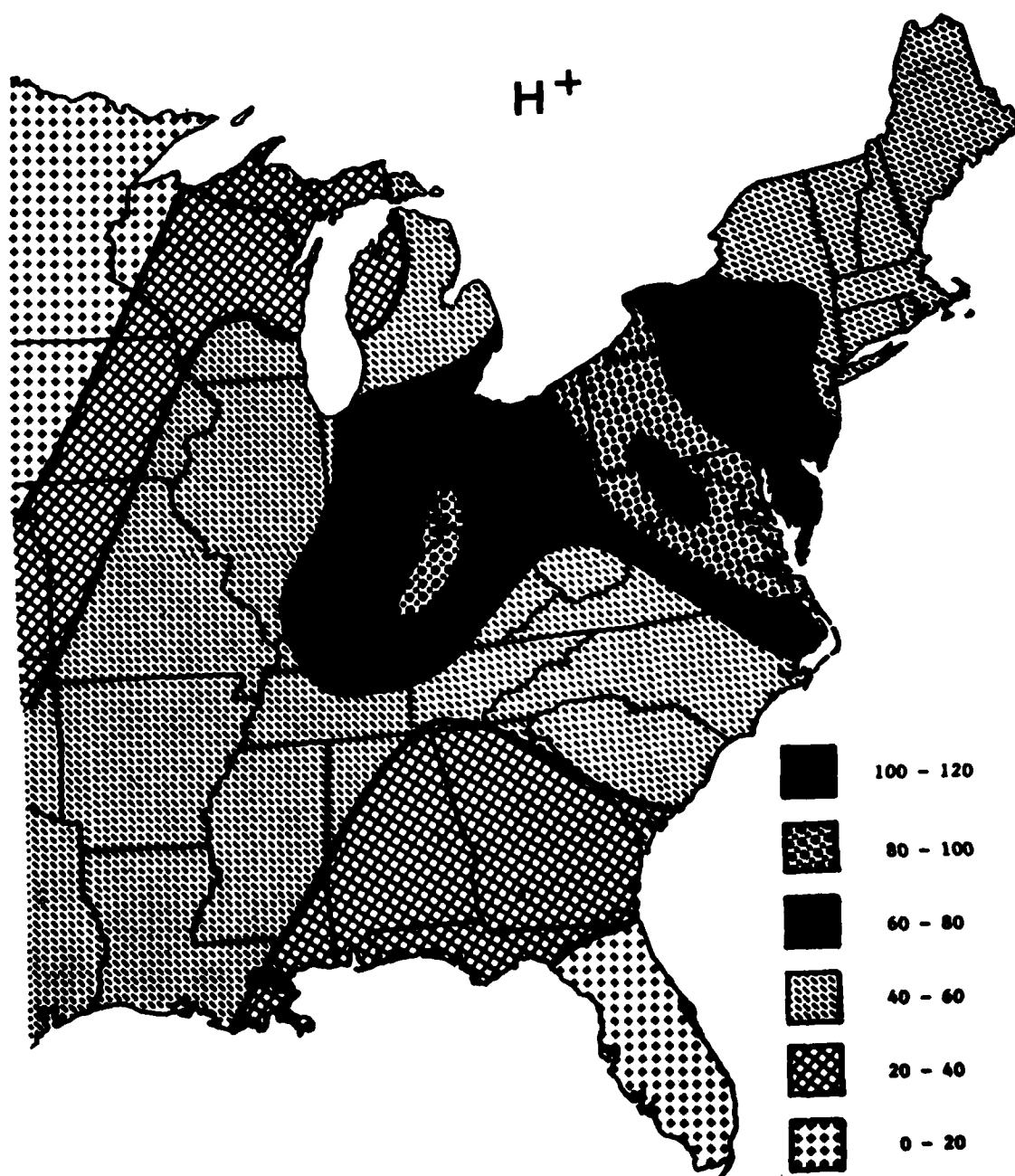


Figure 77. Estimated total H^+ deposition (mg/m^2) for 1979.

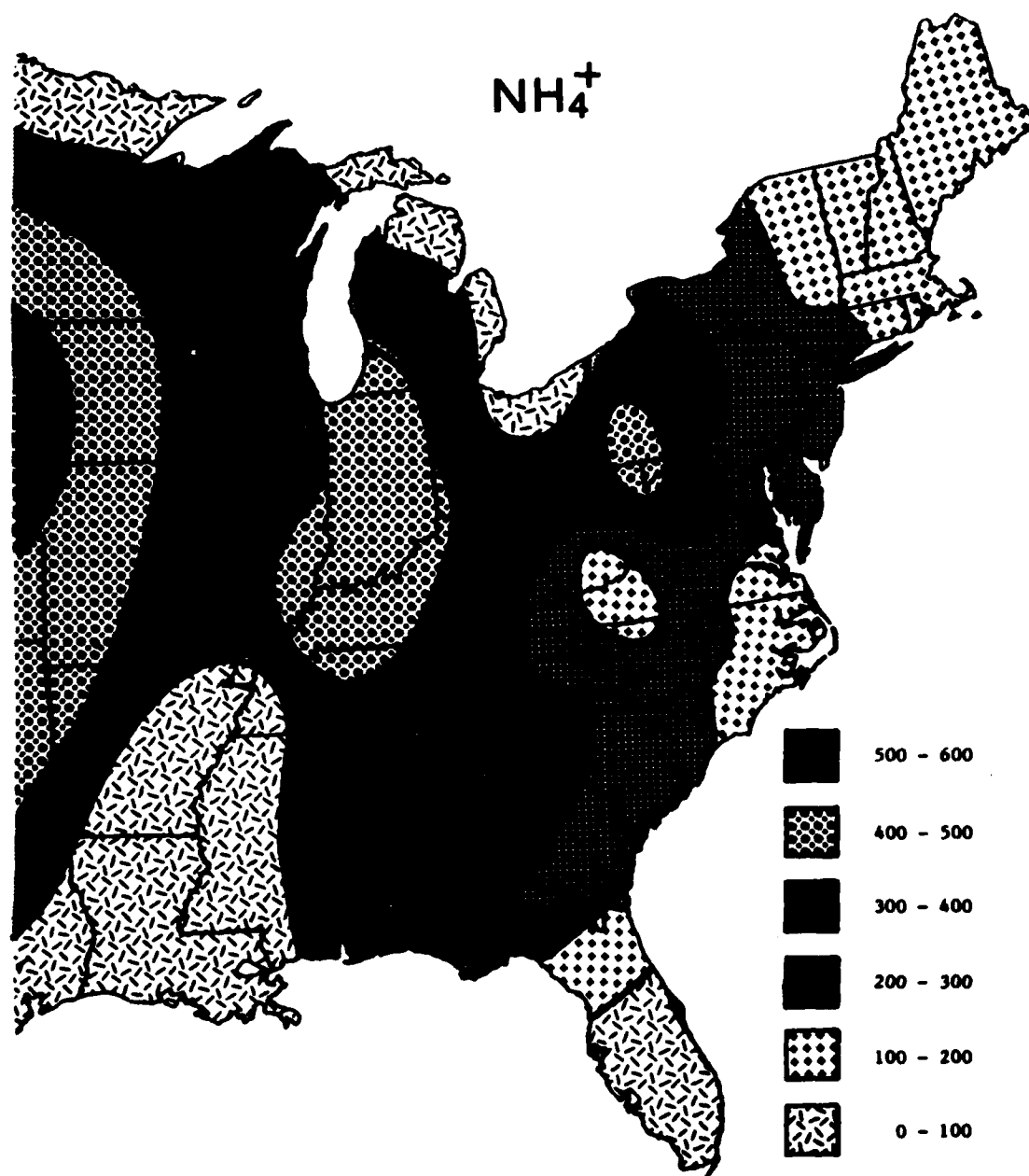


Figure 78. Estimated total NH_4^+ deposition (mg/m^2) for 1979.

regions of increased deposition in western Pennsylvania and the lower Hudson Valley of New York State.

While not an absolute measure of total ion deposition, these wet deposition estimates do provide reasonable approximations. A more dense network, operating over a longer time period, is needed to verify actual total wet deposition on a regional scale of less than 100 km grid space.

It is important to recognize that wet deposition events reported here do not include fog, dew, direct cloud droplet interception, etc. that might give rise to anomalous localized deposition patterns. Those "special deposition events" might play a significant role in mountainous regions, such as the Adirondack Mountains. However, current networks do not measure such events.

5.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 Conclusions

The MAP3S and NADP networks were found to provide a detailed precipitation chemistry data base which may be used to examine event, monthly, and annual deposition of various ions. Wet deposition of the four ions, $\text{SO}_4^{=}$, NO_3^{-} , H^{+} , and NH_4^{+} , that are dominant in precipitation of the northeastern United States, was examined to determine temporal, directional, and spatial variability.

The cumulative wet deposition total was found to be essentially linear over the three-year period for all ions. The concept of a normalized wet deposition, or deposition per unit amount of precipitation was developed and used to estimate long-term deposition over a period of several years. These cumulative deposition estimates are based on historical data, assuming a relatively constant emission pattern and rate. They should not, therefore, be used for predicting the chemical quality of individual events or for short time periods (less than one year).

An approximate ion balance was found to exist in the northeastern United States between $[\text{H}^{+} + \text{NH}_4^{+}]$ and $[2(\text{SO}_4^{=}) + \text{NO}_3^{-}]$ for both the individual precipitation events and the overall period of investigation - 1977-1979.

This overall ion balance of dominant ions, expressed as the cation/anion ratio, approximated one for all MAP3S stations individually and collectively as the regional average. While the sum of the positive and negative ions involving H^{+} , NH_4^{+} , NO_3^{-} , and $\text{SO}_4^{=}$ appear to balance, it by no means implies that the above four ions are

the only important ions present in precipitation. To understand precipitation chemistry per se, it is necessary to include--as a minimum--the measurement of soil and ocean related ionic components (Ca^{++} , Mg^{++} , Na^{++} , Cl^- , etc.). For inland stations in the north-eastern United States, the following ions are deposited in decreasing order of concentration: hydrogen, sulfate, nitrate, ammonium. However, for certain events, the precipitation chemistry at coastal stations can be dominated by ocean related ions (Na^+ , Cl^- , etc.). For stations in the midwest or western part of the United States, the above expressed ion dominance need not be the same. Indications are that the precipitation quality in many parts of the United States can be strongly influenced by soil emissions such as ammonia, calcium and magnesium. The important parameters governing precipitation quality obviously include the alkalinity or acidity of the soil, the type of vegetation, the physical condition of the soil, etc.

The total annual wet deposition was found to be influenced by significant events or "deposition episodes." An analysis of significant events demonstrated that approximately 10% of the total annual ion wet deposition could be accounted for by a singular event. The occurrence of these episodes did not necessarily coincide with air pollution episodes triggered by a high photochemical activity in the lower atmosphere. No seasonal pattern emerged for the deposition episodes.

Normally, a detailed trajectory analysis of individual events will lead to some basic source-receptor relationships. The ionic concentration of individual events was often higher for air masses

having travelled over the Midwest/Ohio Valley during the past 48 hours than for those having passed over the Canadian/Great Lakes region. However, it was also found that elevated levels of ion concentration in precipitation could not always be linked to major pollutant emission regions, nor could "clean" events be necessarily correlated with low pollution areas. This lack of correlation indicates that vital information is still missing on the overall transport-transformation processes that take place in the atmosphere relevant to the formation and deposition of acidic material.

A different picture emerges in regard to the directional variability of wet deposition. Here it was found that the wet deposition of pollution-related ions ($\text{SO}_4^{=}$, NO_3^{-} , and H^{+}) is apportioned between Canadian/Great Lakes sector and the Midwest/Ohio Valley sector according to the percent of annual precipitation contribution from the respective sectors. The annual wet deposition of ions from "Midwest/Ohio Valley air" and "Great Lakes/Canadian air" does not reflect the very significant difference in emission sources that are located in these two regions. The Illinois results further substantiate the above findings. It was also found that the total annual precipitation volume, more than any other single factor, determines the amount of deposition for the three pollution-related ions. Since the majority of the trajectories of precipitation-producing systems were southwest in origin, the preponderance of total deposition was therefore associated with the southwest sector for both stations.

The concept of a "superbowl" would explain to some extent the uniformity in directional variability of wet ion deposition in that the final product, i.e., acidic material, is being rather evenly deposited over a very large region. It would indicate that intense mixing on a synoptic scale, coupled with as yet unknown rate controlling steps for the formation and deposition of acidic material are as important, or more important, than the simple air mass trajectories currently in use. As a result, the known source regions for precursor gases to acid rain cannot yet be unequivocally linked to receptors with the meteorological, physical and chemical information available today.

Spatial variability in wet deposition for the eastern United States was found to exhibit no significant west-east gradient for sulfate and nitrate. Maximum and minimum in normalized wet deposition varied by less than a factor of 1.5 for most of the northeastern United States. A northwest-southeast gradient was found to exist parallel to the Appalachian Mountain chain. This deposition gradient could be the result of orographic blocking of low-level concentrations of SO_2 and NO_x from dispersing into the southeastern region.

Again the concept of a "superbowl" can be used in the absence of a source-receptor relationship (emission-deposition relationship) to explain the relatively uniform wet deposition distribution patterns. The regional uniformity in wet deposition of sulfate and nitrate ions as was found here was also documented in the European Atmospheric Chemistry Network. Granat (1978) reports that the sulfate concentration seems to be comparably little affected by local contamination,

and the large-scale concentration field also seems to be rather smooth. Granat goes as far as to conclude that "the sulfate shows a rather uniform deposition pattern over Europe."

The normalized hydrogen ion deposition demonstrated a much stronger gradient west of 85° longitude (7 to 1) than to the east (2 to 1). The hydrogen ion deposition appears to be affected by locally produced soil derivatives (calcium, magnesium, ammonia, etc.). Interpretations of the hydrogen ion deposition distribution may be erroneous if this fact is not taken into consideration.

Transportation and distribution of the acidity of precipitation is therefore much more uncertain than that of the sulfate concentration. As mentioned earlier, it is likely that the hydrogen ion deposition values are greatly influenced by the physical and chemical condition of the regional soil, as was hinted by Granat (1978).

Since the annual wet deposition pattern shows a rather uniform pattern over a large portion of the eastern United States, it appears as if the emissions and deposition are essentially decoupled: a simple source-receptor relationship is not yet discernible from the existing meteorological and chemical data base.

5.2 Recommendations for Future Research

Trajectory analysis can best be applied when detailed meteorological and chemistry data are available in conjunction with discrete event sampling. The best application of air mass trajectory analysis would be the collection of six-hour precipitation chemistry samples centered on the ARL-ATAD analysis times of 00Z, 06Z, 12Z, and 18Z. This technique would allow a history of the relative contributions

by various approach sectors and provide greater insight into source-receptor relationships and chemical transformation processes.

While this study provides a detailed analysis of wet deposition, the total deposition budget is still unclear. The percentage contribution of wet and dry deposition as well as that by fog, dew, cloud water, and other special events, to the total sum must be understood before the relative importance of each can be identified.

In this study wet deposition within the atmospheric boundary layer is examined. To identify completely and understand transport and transformation mechanisms, measurements should be taken above the boundary layer, free of contamination by locally-produced trace gases and particles. An understanding of microphysical and chemical processes involved during cloud droplet growth and coalescence and precipitation development is essential for characterizing individual precipitation events. Collection and analysis of cloud water from airborne and fixed platforms atop mountains would be necessary to accomplish this task. With this data base at hand, models could be developed and verified that are capable of describing the actual homogeneous and heterogeneous chemistry responsible for transformation of sulfur and nitrogen compounds into sulfate and nitrate ions observed in precipitation.

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